U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-293 253

Characterization of Solid Constituents in Blackwater Effluents from Coal Preparation Plants

Pennsylvania State Univ, University Park

Prepared for

Environmental Protection Agency, Washington, DC Office of Research and Development

Jan 79

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. FE-9002-1(EPA-600/7-79-006)	2.	3. RECIPIENT'S ACCESSION NO. PB293253
4. TITLE AND SUBTITLE Characterization of Solid Constituents in Blackwater Effluents from Coal Preparation Plants		5. REPORT DATE January 1979
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) P. B. Bradley, F. F. Aplan and R. Hogg		8. PERFORMING ORGANIZATION REPORT NO. DoE FE-9002-1
9. PERFORMING ORGANIZATION NAME AND ADDRESS Pennsylvania State University University Park, Pennsylvania 16802		10. PROGRAM ELEMENT NO. EHE623A
		11. CONTRACT/GRANT NO. EPA Interagency Agreement DXE685AK
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 7/75 - 10/77
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer: D. A. Kirchgessner, MD-61, 919/541-2851. DoE project offi A. F. Baker), Div. of Solid Fuel Mining and Preparation, Pittsburgh PA 15213.

16. ABSTRACT

The report gives results of a characterization of the fine solid constituents of coal preparation plant waste water, to provide a better understanding of how to treat the water for recycle or discharge. Thirteen waste water samples, obtained from coal preparation plants throughout the U.S., were analyzed for: identification and quantification of solid constituents, size analysis of solids, and surface properties of the solids. The study concluded that: (1) Eastern and Western coal region samples can be distinguished on the basis of mineralogy and size distribution of the solid particles; (2) the carbonaceous material of Eastern coals averages 60% of the blackwater solids, and the remaining 40% consists of clay minerals, quartz, calcite, and pyrite; and (3) virtually all of the carbonaceous material in Eastern plant waste waters can be removed by froth flotation, with the product containing 11% mineral matter.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Quartz	Pollution Control	13B	
Coal Preparation	Calcite	Stationary Sources	08I	
Waste Water	Pyrite	Blackwater		
Particle Size Distribution		Mineralogy		
Carbon	Flotation	Particulate	07B	07A, 13H
Clay Minerals	Froth		08G	11G

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 203
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PC A10 / MF A01

☆ U.S. GOVERNMENT PRINTING OFFICE: 1979—640-092/474

PB 293253

DoE

United States
Department of Energy

Division of Solid Fuel
Mining and Preparation
Pittsburgh PA 15213

FE-9002-1

EPA

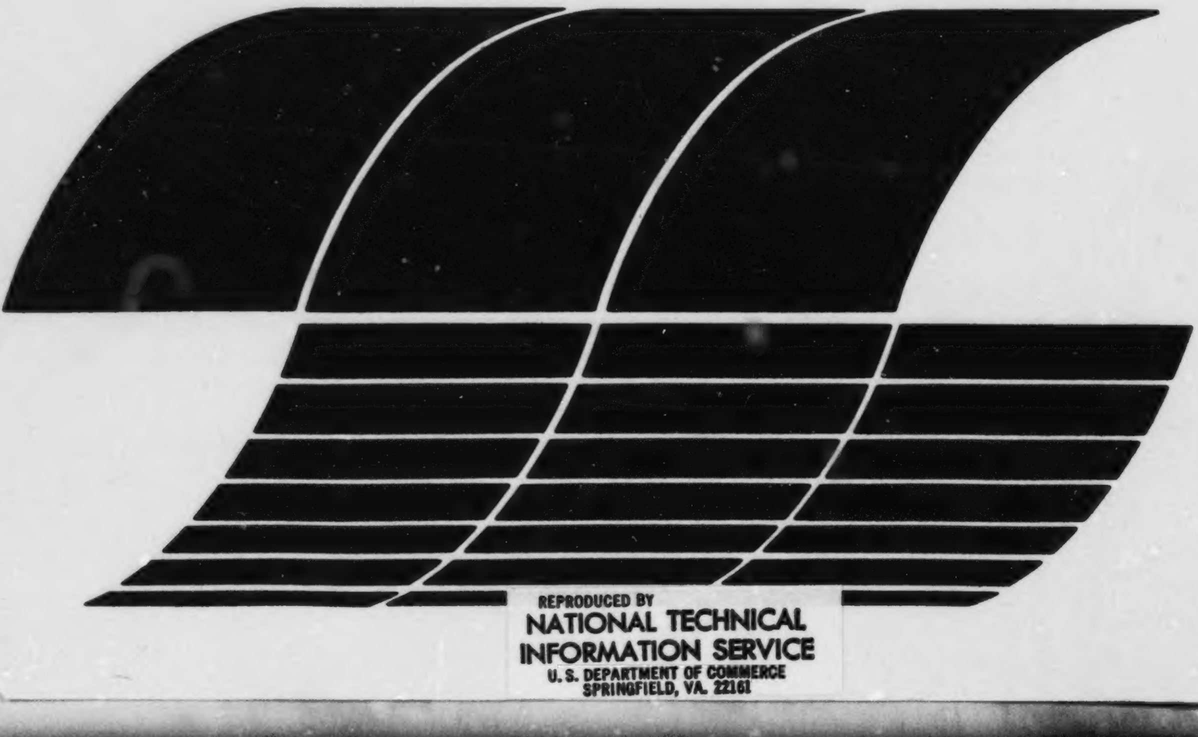
U.S. Environmental Protection Agency
Office of Research and Development

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-006
January 1979

Characterization of Solid Constituents in Blackwater Effluents from Coal Preparation Plants

Interagency
Energy/Environment
R&D Program Report



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Price: Paper Copy $9.25
Microfiche $3.00

FE-9002-1
(EPA-600/7-79-006)
January 1979
Distribution Category UC-90b

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EPA/DoE Interagency Agreement No. DXE685AK
Program Element No. EHE623A

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

and

U.S. DEPARTMENT OF ENERGY
Division of Solid Fuel Mining and Preparation
Pittsburgh, PA 15213

1a

Final Project Report, Part I

U.S. Department of Energy

Project No. ET-75-G-01-9002

Characterization of Solid Constituents from Blackwater Effluents from Coal Preparation Plants

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June 1977

ACKNOWLEDGEMENTS

The authors wish to acknowledge Mr. Michael Placha, currently with Birtley Engineering Corporation for his invaluable effort in the development of the separation and sizing techniques and for performing several of the size analyses described in this report.

Special thanks are also due to those companies who supplied the black water samples.

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I. INTRODUCTION

In 1973, 289 million tons of clean coal were produced by mechanical cleaning from 398 million tons of raw coal in approximately 400 coal preparation plants throughout the United States (37). The majority of these facilities is located in the Eastern coal producing areas of the United States, principally in the Appalachian region. Assuming that 3 percent of the raw coal (2) processed in coal preparation plants will report to some form of slurry or tailings treatment, then approximately 12 million tons of slimes on a dry basis were produced during the cleaning process in 1973. It is this fine material which is suspended in the waste water - the "blackwater" of coal preparation plants - that has to be treated in a manner that meets environmental regulations.

In the past, blackwater usually was treated by flocculation and thickening with the thickener underflow being pumped to slurry ponds for final disposal, or, alternatively, the blackwater was sent directly to the slurry pond without thickening or clarification. The clarified or partially clarified water from the thickener and/or slurry ponds was either recycled to the plant for additional use or discharged to a stream. The new environmental regulations concerning process water from coal preparation plants states: "There shall be no discharge of pollutants from coal preparation plants" (10). The government is stressing the use of closed water circuits as a means of achieving this "no discharge" regulation. These regulations make it very difficult to obtain approval to use slurry ponds, and in most cases the government insists on a closed water circuit that excludes the use of slurry ponds to dewater thickener underflow (13).

Obtaining a closed water circuit for some preparation plants may be expensive since this could involve modification or installation of additional treatment processes such as froth flotation, flocculation, clarification, filtration, centrifugation, etc. Furthermore, in order to comply with the government regulations, a high degree of reliability will have to be obtained in the water treatment system, and this will undoubtedly involve additional capital and operating expenditures.

One of the principal methods of concentrating fine solids in the plant discharge water has been to allow the suspended particles to settle in a thickener. The thickener overflow is then recycled back to the plant water system. In order to achieve good thickener efficiency, inorganic and organic flocculants have traditionally been added to the feed slurry. This procedure not only increases the settling rate of the fine particles, but the flocculants also serve to clarify the thickener overflow to be recycled. The effectiveness of the different flocculants and their costs vary substantially from plant to plant. Pritchard (31) in 1974 compared the cost of flocculants at two different plants and found the following costs:

Kentucky Mine Flocculant Cost

3-1/4 cents/ton of total cleaned coal
22 cents/ton of minus 28 mesh cleaned coal

Southern West Virginia Mine Flocculant Cost

27 cents/ton of total cleaned coal
$2.00/ton of minus 28 mesh cleaned coal

Thus, there can be a large variation in flocculant cost from one plant to another, but, in any event, flocculation costs are by no means a negligible part of the total preparation costs. There are many possible explanations for this great variation in the costs for flocculating blackwater from different sources, but mineralogical and size differences most probably account for most of these differences. For example, in the cases cited, the run-of-mine coal from the Kentucky mine had an ash content of 15 percent, while the West Virginia coal contained an ash content of 45 percent in the run-of-mine coal.

The purpose of this study is to characterize the fine solid material in the waste water so that a better understanding of the problems associated with treating "blackwater" may be obtained. The three areas selected for investigation were: identification and quantification of the solid constituents, size analysis of the particulate material, and an investigation of the surface properties of the solid material. Thirteen samples of waste material from coal preparation plants throughout the United States were analyzed. The samples were so selected as to be representative of the discharge from preparation plants treating coal from major coal seams in the country. These samples were obtained from both surface and underground mines and from plants with a wide variation in preparation circuit complexity.

II. BACKGROUND AND THEORY

A. Introduction

The purpose of this study was to characterize the fine solid material in the primary effluent from coal preparation plants so that a better understanding of the problems associated with treating "blackwater" could be obtained. In this study "blackwater" is defined as the aqueous, fine particle-containing, primary effluent from a coal preparation plant. The composition of this effluent is highly variable depending on the coal seam mined, the mining method, and the preparation procedure employed. Due to differences in the nature of the material mined and the extent of fine cleaning practices in a particular plant, the fine particulates contained in the discharge water may range anywhere from predominately coal to predominately mineral matter. The size consistency of the particulates is generally 28 mesh or finer. Those older plants employing only crude preparation processes may send all of the minus 28 mesh material to the refuse slurry pond and this material will therefore contain a substantial percentage of coal. On the other hand, modern preparation plants with extensive fine cleaning circuitry, and employing froth flotation, may discharge only a minimal amount of combustible material and the blackwater effluent will contain largely high ash particles generally less than 200 mesh in size. The composition of blackwater is thus highly variable.

The primary blackwater effluent is typically sent to a solid/liquid separation unit such as a thickener or slurry pond and the water is removed for recycling. Settlement of the solids is normally assisted through the addition of a flocculant to improve clarity of the recycled water, increase the settling rate of the particulates, improve settled sludge density, and minimize the capital investment of the solid/liquid separation unit. A basic understanding of the particulate material being treated, its mineralogical composition, size distribution, and surface properties is essential to the effective design of any flocculation process.

B. Overview of Coal Preparation

The type of coal preparation used at any particular site depends on a number of factors, including such things as market conditions, characteristics of the coal, and mining methods. Coal is usually treated in stages with the coarse coal being cleaned in a different manner than is the fine coal (20). The most commonly employed coal cleaning methods are those using water, and the amount of water used varies considerably from one method to another. This is clearly shown in Table 1. Generally, the fine cleaning methods require more water per ton treated than do modern coarse cleaning methods. Inherent in the type of material being treated, the discharge water from the fine cleaning units tends to have more fine solids suspended in it than does the waste water from coarse cleaning units. Therefore, a plant which is treating a relatively high

Table 1. Water used in various coal cleaning operations. (after Lucas, Maneval, and Foreman [21])

Coal Cleaning Unit	Size Range of Feed		Feed		Conc	Tails	
	Anthracite	Bituminous	Max tph	% Solids	% Solids	% Solids	GPH H_2O tph Feed
Baum Jig	8"-1/8"	8"-1/8"	1-5tph/ft^2	85-90	Dewatered	Dewatered	3-5 (recycled)
Chance Cone	8"-1/16"	8"-1/16"	50tph/ft^2 (425)	85-90	Dewatered	Dewatered	7-12 media
Hydroseparator	5"-1/32"	5"-1/2"	4tph/in. (190)	85-90	Dewatered	Dewatered	14-18
Menzies Cone	5"-1/32"	5"-1/2"	Anth:160 Bit:300	85-90	Dewatered	Dewatered	14-18
Belknap Washer	None	6"-1/4"	160	85-90	Dewatered	Dewatered	5 (makeup)
Rheolaveur Sealed Discharge	4"-1/4"	4"-1/4"	8-10tph/in	15-30	Dewatered	Dewatered	6-12
Hydrotator	2"-0"	2"-0"	5tph/ft^2 (320)	85-90	Dewatered	Dewatered	12-16
DSM Cyclone (as heavy media)	3/4"-20-48M	1/4"-0"	5-35	12-16	Dewatered	Dewatered	20-30 media

Table 1. Continued.

Coal Cleaning Unit	Size Range of Feed		Feed		Conc % Solids	Tails % Solids	GPH H_2O tph Feed
	Anthracite	Bituminous	Max tph	% Solids			
Humphrey Spiral	1/4"-200M	1/4"-200M	1.0-1.5	15-20	12-25	15-40	30
Conc Table	1/4"-0"	1/4"-0"	10-15	15-25	10-20	20-35	12-16
Rheolaveur Free Discharge	1/4-0"	1/4"-0"	3-5tph/in	15-30	Dewatered	Dewatered	3-4
Flotation Cell	28Mx200M	48Mx200M	2-4	20-30	35-60	10-20	13-16

percentage of fine coal will most probably have a more difficult water treatment problem.

Modern, efficiently designed and managed coal preparation plants typically produce a water containing 35 mesh x 0 solids, with the minus 325 mesh content, by weight, ranging from 35 to 80 percent, frequently tending toward the latter (2). The primary blackwater effluent from coal preparation plants is usually treated initially by flocculation techniques in conjunction with a thickener. A typical thickener feed contains 1-5 percent solids by weight and the thickener underflow will normally contain 20-35 percent solids by weight (34).

The common types of flocculants used to treat blackwater are inorganic electrolytes such as lime and alum, and organic polymers such as starches and synthetic polymers (e.g., polyacrylamide). Thickening of coal refuse slurries is usually accomplished by using high molecular weight organic flocculants that provide rapid settling of most of the solids (6). The synthetic polymers cost more per pound than do many of the natural polymers, but their ability to produce comparative flocculation results at relatively low concentrations makes them very economical.

The thickener underflow, consisting of the flocculated and settled solids, can be treated by a number of different methods such as those listed in Table 2.

Table 2. Possible methods of treating thickener underflow. (after Gregory [13])

Impoundment

Underground pumping

Mechanical dewatering

Incineration

Chemical mixing

Spherical agglomeration

Pelletizing

Thermal drying

A preparation plant closed-water circuit is desirable in order to comply with environmental regulations concerning the quality and quantity of water discharge, and to achieve the economies, which result from the efficient re-use of the large amount of water required for coal preparation. In achieving a closed-water circuit system for a coal preparation plant, operators strive to have no discharge of blackwater, to minimize the build-up of solids in the recirculated water, and to separate the solids from the primary blackwater slurry in a form suitable for transport and disposal in a stable, permanent form that is environmentally acceptable and legal.

C. Overview of Flocculation

Solid particles suspended in water can be concentrated by allowing the particles sufficient time to settle. Under relatively quiescent conditions, fine particles will concentrate by settling due to gravitational forces, but the rate at which particles settle is dependent on a number of factors, one of which is particle size. The rate of free settling for fine particles suspended in water is described by Stokes' Law:

$$V_m = \frac{(\rho_p - \rho_L) d_p^{\,2} g}{18\mu} = \frac{s}{t}$$

V_m = maximum settling velocity

ρ_p = density of particle

ρ_L = density of liquid

d_p = diameter of particle

g = gravitational acceleration constant

μ = viscosity of liquid

s = distance

t = time

Analysis of Stokes' Law shows that the rate of settling depends on the square of the particle diameter. Under the same conditions, the time to settle a 1 μm particle will be 10,000 times longer than the time to settle a 100 μm (150 mesh) particle of the same density. Thus, for very fine particles, the use of settling basins to concentrate the suspended solids becomes impractical for commercial operations due to the enormous size of the basins that would be necessary to obtain long retention times.

The fine particles, with their extremely slow settling rates, can be settled at a much higher rate if the particles are agglomerated to form large particles which settle at a much faster rate. Fine particles can be agglomerated using established flocculation techniques. Agglomeration of fine particles involves particle-particles collisions of sufficient energy for van der Waals forces to take effect and cause agglomeration.

The surface of suspended particles develop an electrical charge due to imperfection in crystal structure and/or by the preferential adsorption of certain ions (38). In the formation of many naturally-occurring minerals, especially alumina silicates, isomorphous substitutions (of Al^{+3} for Si^{+4} or Mg^{+2} for Al^{+3} for example) are common. These substitutions can lead to a net charge on the crystal lattice. Fractured surfaces on particles produced by breakage of larger fragments can also acquire an electrical charge. In this case, the existence of unsatisfied valences at the surface causes the adsorption of various species from solution. If certain ions are adsorbed preferentially, a charge will be developed on the surface. The charge on clay particles is a result of both of these effects: crystal imperfection and broken bonds.

When the surface charge on a particle results from preferential adsorption, its sign and magnitude can be varied by changing the concentration of those ions in the solution. The ions responsible for the charge development are known as the potential-determining ions for that particular material (38). Since hydronium and hydroxyl ions are potential determining for many insoluble oxide minerals and coal (3,8), the sign and magnitude of the charges on the surface are pH dependent. At a certain pH, the adsorption of hydronium and hydroxyl ions is equal and the net charge on the surface is zero. This condition is referred to as the pH of the "point of zero charge," (PZC) for that mineral.

As a result of the surface charge, a diffuse layer of ions, of change opposite to that of the surface, accumulates in the liquid near the particle surface creating an electrical double layer which compensates for the surface charge of the particle. The thickness of the double layer is inversely related to the ionic concentration of the solution. If the ionic concentration is small then the thickness of the double layer will be large and vice versa for concentrated solutions. Thus, the thickness of the double layer of a charged particle may be varied by varying the total ionic strength in the suspending fluid.

The magnitude and sign of the surface charge and the thickness of the double layer will have a definite effect on the rate of agglomeration of particles in a suspension. Particles of similar sign will repel each other and as the magnitude of the charge increases, the repulsion will increase making agglomeration more difficult. The magnitude of the surface charge on an oxide mineral or coal can be reduced by adjusting the pH of the solution in order to decrease the surface potential and thus increase the ease with which the suspension may be flocculated. The thickness of the double layer also affects the rate of agglomeration. Particles with thick double layers are held too far apart for van der Waals forces to take effect during particle collision and flocculation can only occur very slowly. The double layer thickness can be reduced by increasing the ionic concentration in the suspension, thus the rate of flocculation can be increased by adding inorganic and/or organic electrolytes to a suspension (28).

Certain organic polymers are highly effective flocculants; several mechanisms have been proposed to account for their action. If the flocculant is a polyelectrolyte, charge neutralization, double layer compression, etc., can occur as for inorganic electrolytes. A bridging mechanism was advanced by Healy and LaMer (15). In this model, the polymer molecules are considered to adsorb irreversibly on the surface of the particles. Each polymer molecule adsorbs to two or more particles forming a "bridge" between them. The flocs produced by the polymer settle at a faster rate than the individual particles. Another proposed mechanism for the action of polymeric flocculants is the "enmeshment" model advocated by Vanderhoff (39). In this model the long chain polymer molecules interlock in a sort of net and entrap particles either by attachment or by enmeshment. These added features, bridging and enmeshment, of organic polymers makes them a very effective means of flocculating fine particles. Thickening of coal refuse slurries is usually accomplished with high molecular weight organic flocculants that provide rapid settling of most solids but, not infrequently, may leave some of the finer particles still suspended (6).

Characterization of the properties of a suspension to be flocculated should be very helpful in optimizing fine particle flocculation in that system. Particle size distribution, mineralogical classification, and surface properties should be known to obtain a basic understanding of the flocculation mechanisms taking place.

D. Ash-Forming Minerals in Coal

An estimation of the mineral matter contained in blackwater may be obtained from the composition of the mineral matter found within a coal seam. The identification of ash-forming minerals commonly found in coal, as reported by Nelson (25) is shown in Table 3. The mineral constituents were not quantified in Nelson's report, but certain minerals occurred more frequently and in larger quantities than others. These important minerals, in the judgment of the author of this thesis, have been underlined in Table 3.

Table 3. Minerals found in coal. (after Nelson [25])

Shale Group:	Illite, Montmorillonite, Bravaisite, Hydromuscovite, Muscovite
Kaolin Group:	Kaolinite, Levisite, Metahalloysite
Sulfide Group:	Pyrite, Marcasite
Carbonate Group:	Calcite, Siderite, Dolomite, Ankerite
Chloride Group:	Sylvite, Halite
Accessory Minerals Group:	Quartz, Gypsum, Chlorite, Rutile, Hematite, Magnetite, Sphalerite, Feldspar, Garnet, Hornblende, Apatite, Zircon, Epidote, Biotite, Augite, Prochlorite, Diaspore, Lepidocrocite, Barite, Kyanite, Staurolite, Topaz, Tourmaline, Pyrophyllite, Penninite

Table 4. Mineralogical composition of anthracite refuse. (after Augenstein and Sun [5])

	Mineral Constituents, % Mineral Matter					
Sample	Illite	Kaolinite	Pyrophyllite-Kaolinite	Quartz	Pyrite	Rutile
Von Storch	40.8	35.0	---	20.8	1.7	1.7
Powderly	45.9	38.9	---	12.4	0.7	2.1
Blue Coal	37.4	36.9	---	22.4	1.7	1.6
St. Nicholas	41.1	---	44.3	9.9	3.3	1.4
Oak Hill	34.6	---	51.6	10.6	1.8	1.4
Westwood	38.8	36.9	---	21.6	1.2	1.5
Hazelton Shaft	39.7	34.9	---	22.6	1.1	1.7

Augenstein and Sun (5) studied the mineral composition of Pennsylvania anthracite refuse and their data are shown in Table 4. These data indicate that anthracite refuse is typically composed of about 40 percent each of illite and kaolinite, or pyrophyllite-kaolinite clays and 10-20 percent quartz, with smaller amounts of pyrite and rutile.

More recently, O'Gorman and Walker (27) have made a comprehensive study of the mineral matter contained in lithotypes from major United States coal seams using x-ray diffraction and infra-red spectroscopy. They also made a semi-quantative analysis of the mineral matter of each of these coal samples. Table 5 is a statistical summary of their findings adapted from their extensive data. Note that while the variation between samples is great (range), the principal mineral present, on the average, is kaolinite together with lesser amounts of illite, quartz, and gypsum. It is interesting to note that calcite did not occur in significant amounts in most of the samples analyzed but gypsum did. It should be cautioned that the O'Gorman and Walker data were obtained mostly from hand-picked lithotypes of coal containing but little ash. Their data thus represent the mineral matter contained in coal, essentially the inherent ash-forming minerals. Furthermore, because their study represents the majority of United States coal seams presently being mined, it is, in fact, largely a study of the mineral matter of coals dating from the Pennsylvanian Period since this is the geologic period in which the Appalachian and Mid-continent coal fields were formed.

Table 5. Average mineralogical composition of ash forming constituents in major U.S. coal seams. (modified after O'Gorman and Walker [27])

Mineral	Mean	Standard Deviation	Range
	%	%	%
Kaolinite	34.8	23.6	0-85
Illite	7.8	8.5	0-35
Montmorillonite	0.7	1.3	0-10
Mixed Layer Illite - Montmorillonite	3.2	2.3	0-20
Chlorite	1.5	1.5	0-10
Quartz	10.1	10.1	0-40
Gypsum	11.9	13.0	0-60
Rutile	2.3	1.3	0-10
Others Pyrite, siderite, dolomite, calcite, aragonite, ankerite, muscovite, plagioclase, hematite, jarosite, thenardite			

Because the O'Gorman and Walker study deals mainly with the analysis of interspersed mineral matter in coal lithotypes, it may not represent the mineral composition of run-of-mine coal. The mineral matter in run-of-mine coal will be influenced by both the inherent mineral matter of the coal and the more segregated mineral matter which comprises the high ash constituents associated with the coal, especially those near the edges of the seam. Thus, overbreak during mining, which may incorporate ash-forming minerals from the adjacent strata into the coal coming from the mine, will contribute in a major way to the material which eventually makes up the black water. The composition of the blackwater is thus not only a function of the mineral matter inherent in the coal seam, but is influenced in a more important way by the mineralogical composition of the adjacent strata when overbreak is substantial.

Then, too, there is a further complication in that the mineral matter, either within the coal seam or adjacent to it, will degrade in different ways during the preparation process. The fine particulates contained in the blackwater will obviously come largely from those ash-forming constituents that degrade most readily.

The need to obtain a mineral analysis of the actual blackwater constituents is the reason for this study. The samples were selected so as to be representative of the discharge from preparation plants treating coal from major United States coal seams.

III. EXPERIMENTAL MATERIALS AND METHODS

A. Samples

Thirteen samples of waste material from coal preparation plants throughout the United States were selected for study (see Table 6). The blackwater samples were classified into two main groups--Eastern, Samples 1-11, and Western, Samples 12 and 13--based on differences in the nature of the solid material as a result of geologic genesis. Samples 1 through 11 were obtained from thickener underflows, or slurry pond feed, with the first nine samples received in slurry form and Samples 10 and 11 received in dry form. Sample 12 was obtained from a settling pond and Sample 13 from a refuse conveyor belt. In order that it correspond approximately to the rest of the samples, the Sample 13 refuse was wet screened over a 28 mesh sieve and only the minus 28 mesh fraction retained for study. The majority of the samples were from Appalachian coal fields since this area contains the majority of preparation plants in the United States. An attempt was made to obtain at least one sample from each of the major coal areas which use wet preparation. Western sub-bituminous and lignite coal samples were purposely excluded since they are not treated by wet preparation methods.

Table 6. Blackwater samples tested.

	Identification		
Identification Code[a]	Seam	County	State
Eastern			
Pi. W Pa 1	Pittsburgh	Washington	Pennsylvania
L.K. C Pa 2	Lower Kittanning	Cambria	Pennsylvania
L.K. C Pa 3	'B' Lower Kittanning	Cambria	Pennsylvania
L.F. C Pa 4	"D" Lower Freeport	Cambria	Pennsylvania
Po. M WVa 5	#3,4,5 Pocohontas	McDowell	West Virginia
Po. W WVa 6	#3 Pocohontas	Wyoming	West Virginia
Pi./L.F. H Oh 7	75% Pittsburgh 25% Lower Freeport	Harrison	Ohio
E L Ky 8	#2 Elkhorn	Letcher	Kentucky
Pr. J Ala 9	Pratt	Jefferson	Alabama
I6/5 J Ill 10	#5,6 Illinois	Jackson	Illinois
I6 W Ind 11	#6 Indiana	Worrick	Indiana

Table 6. Continued.

Identification Code[a]	Identification		
	Seam	County	State
Western			
B.D. L Wa 12	Big Dirty	Lewis	Washington
S/L.S. Ut 13	Somerset 'B', 'C' Lower Sunnyside	Gunnison Carbon	Colorado Utah

[a] Identification Code: Seam, county, state, sample number.

B. Identification and Quantification of the Solid Constituents in Blackwater

1. Sample Preparation

Particulate matter in blackwater consists of carbonaceous material and mineral matter. Because of the substantial difference in the properties between the mineral and carbonaceous particles, it was decided to separate the solid material into a mineral fraction and a carbonaceous fraction. Froth flotation (3,7) was used to concentrate the blackwater samples into a froth containing the coal and a tailings fraction composed mainly of the ash-forming minerals. The flowsheet for this separation procedure is shown in Figure 1. The efficiency of the separation was determined by microscopic examination and by ash analysis of the two fractions.

Approximately 25 grams of solids from each blackwater sample were separated using this procedure. The samples were dis-aggregated in a Hamilton Beach, single-speed milkshake blender for five minutes, and then transferred to a 100 gram Denver Flotation Cell. The flotation unit consisted of a Hamilton Beach milkshake blender that was converted into a flotation unit using a kit manufactured by Denver Equipment Division, Joy Manufacturing Company, Denver, Colorado. Air was incorporated into the pulp through the open vortex caused by stirring, and so the speed of the impeller was adjusted to give a sufficient air flow to produce the desired froth. The propeller speed of the converted blender was varied using a

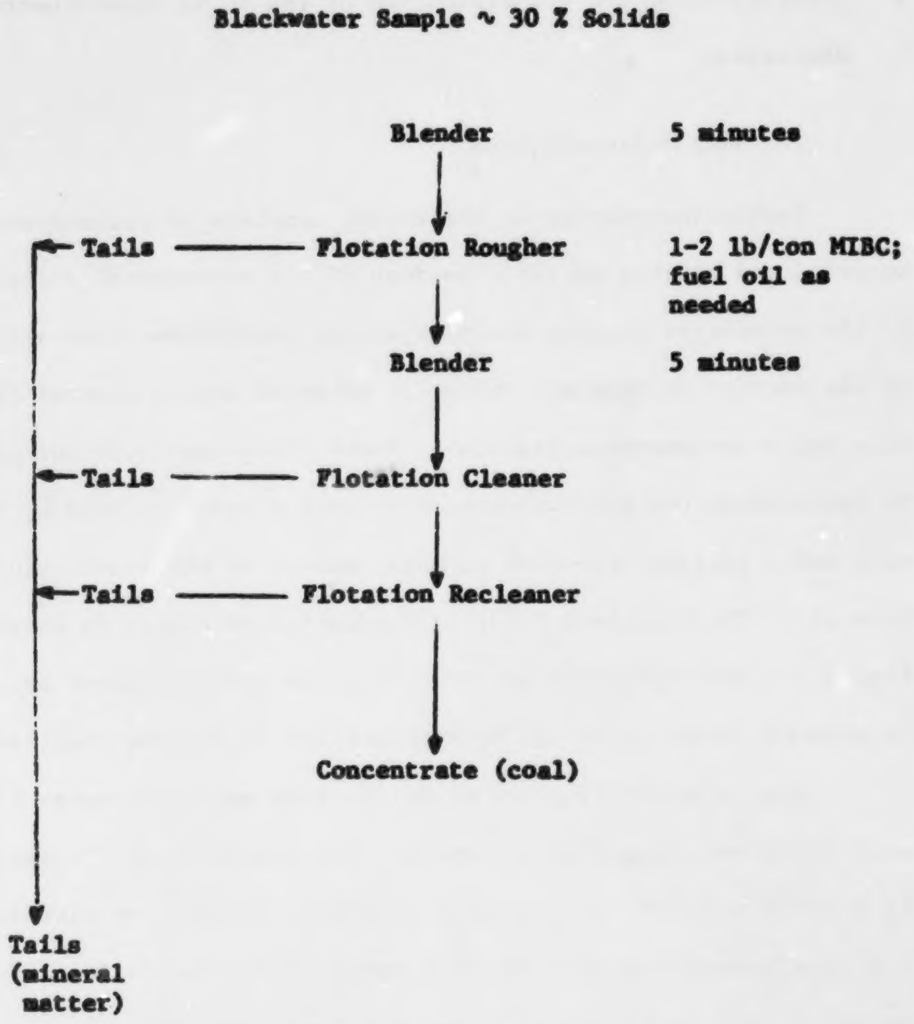
Blackwater Sample ~ 30 % Solids
Blender
5 minutes
Tails
Flotation Rougher
1-2 lb/ton MIBC; fuel oil as needed
Blender
5 minutes
Tails
Flotation Cleaner
Tails
Flotation Recleaner
Concentrate (coal)
Tails (mineral matter)

Figure 1. Flowsheet for froth flotation of blackwater samples.

rheostat. The amount of time and reagents needed to obtain good flotation results for each sample varied depending on the size of the particles and the surface characteristics of the coal. The flotation of coarse and oxidized coal particles was particularly troublesome, and in some cases where large oxidized coal particles were present, the efficiency of separation was not particularly good. In those cases where unfloated coal particles were present in the mineral matter fraction (in amounts never exceeding 10%), the amount of coal was determined microscopically and the appropriate adjustments were made in the analyses. The effectiveness of the froth flotation step was not only estimated by microscopic examination, but also by an ash analysis of the two fractions.

The rougher concentrate was further cleaned by stirring it for five minutes to insure maximum dis-aggregation of coal from the high ash gangue and subjecting it to two more stages of flotation. The final products consisted of a concentrate containing carbonaceous material and a tailings containing the mineral matter.

2. Analysis of Carbonaceous Material

a. Introduction. As previously discussed, froth flotation was used to separate the blackwater samples into separate fractions--a mineral fraction and a carbonaceous fraction. The efficiency of the separation of each blackwater sample was determined by microscopic examination of the fractions and by ash analysis.

b. Ash analysis. Ash analyses were performed on both fractions--mineral and carbonaceous--of each sample. Ash determinations were made using the ASTM D-271 method. A one gram, minus 65 mesh sample was measured into a weighed crucible, and the crucible was then heated to 750°C in a laboratory muffle furnace. The sample was stirred and allowed to remain at 750°C for 1-1/2 hours. After cooling, the crucible and ash were weighed and the ash determined by subtracting the crucible tare.

c. Sulfur analysis. The total sulfur in each sample was determined using a LECO Induction Furnace and Automatic Titration Unit made by Laboratory Equipment Corporation, St. Joseph, Michigan. In this procedure, the sample was ground to minus 65 mesh, heated in a stream of oxygen, and the sulfur dioxide adsorbed into an acidified starch-potassium iodide solution. The resulting solution was titrated with a standard potassium iodate solution. The accuracy of this method has been shown in previous studies (16,32). The mineralogical sulfur source (e.g., pyrite, gypsum) in the mineral fraction was identified by standard x-ray diffraction techniques.

3. Mineral Identification and Quantification

a. Introduction. The mineral matter in the blackwater sample was separated from the carbonaceous material using the flotation procedure previously outlined. Since the tailings product consisted of a very dilute slurry containing the mineral matter, these solids were concentrated by centrifuging the entire suspension. Once the material was concentrated, a representative sample of the mineral matter was removed, dried, weighed, and analyzed by x-ray diffraction.

The mineral composition of each blackwater sample was determined in two ways. In the first method, an x-ray diffraction analysis was made on the representative sample of the mineral matter of each sample. In the second method, the minerals in the mineral fraction were concentrated into different layers by centrifuging a dispersed suspension of the material. The larger, heavier material concentrated at the bottom, while the smaller, lighter particles, which settled more slowly, concentrated in the top layers. The material was removed in separate layers which were then dried, weighed, and their mineralogical composition quantified by x-ray analysis. From the analysis of each layer, an overall mineralogical analysis was calculated. The results of the two methods were used to obtain a range and a mean percent for each mineral.

b. Identification. For identification of the mineral constituents, the material was ground into a fine powder and dispersed with water and spread onto a glass slide. The material was then scanned over the appropriate 2θ range (usually 5° to 40°) using a Philips (Norelco) X-Ray Diffractometer with nickel-filtered copper K α radiation at 40 Kv and 16 ma. The ash-forming minerals were identified using JCPDS standard (19) characteristic values for the interplanar spacing of each mineral. Table 7 lists the x-ray diffraction spacing of each of the minerals which commonly occur with coal.

Table 7. Principal x-ray diffraction spacings of minerals commonly occurring with coal. (after O'Gorman and Walker [27])

Mineral	Diffraction Spacing (Å)
Kaolinite	7.15(100), 3.57(80), 2.38(25)
Illite, Mica	10.1(100), 4.98(60), 3.32(100)
Montmorillonite	12.0-15.0(100)
Chlorite	14.3(100), 7.18(40), 4.79(60), 3.53(60)
Mixed Layer Illite-Montmorillonite	10.0-14.0(100)
Calcite	3.04(100), 2.29(18), 2.10(18)
Dolomite	2.88(100), 2.19(30)
Siderite	3.59(60), 2.79(100), 2.35(50), 2.13(60)
Aragonite	3.40(100), 3.27(52), 1.98(65)
Pyrite	3.13(35), 2.71(85), 2.42(65), 2.21(50)
Marcasite	3.44(40), 2.71(100), 2.41(25), 2.32(25)
Quartz	4.26(35), 3.34(100), 1.82(17)
Gypsum	7.56(100), 4.27(50), 3.06(55)
Rutile	3.26(100), 2.49(41)
Feldspar	3.18-3.24(100)

Relative intensities are shown in parentheses.

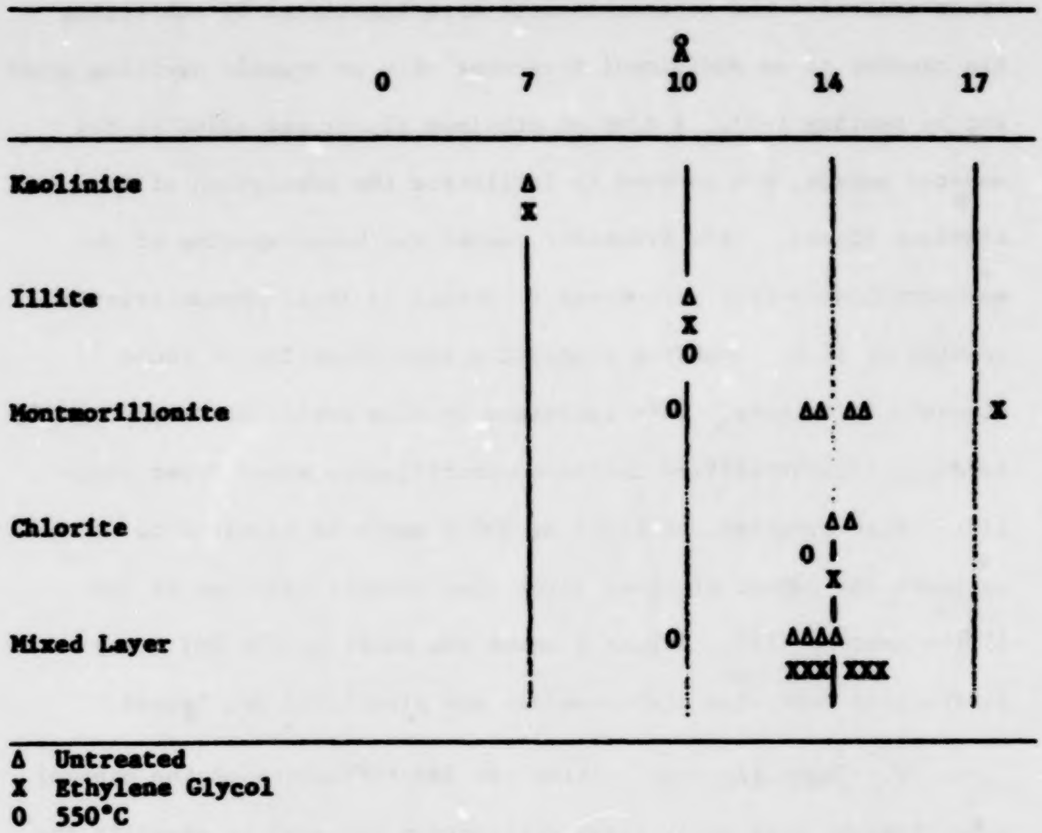

Figure 2. Shift of the 001 x-ray diffraction peak when clay minerals are glycolated and heated. (40)

Expandable layer clays such as interstratified illite-montmorillonite and montmorillonite were identified by subjecting the samples to an additional treatment with an organic swelling agent and by heating (40). A drop of ethylene glycol was added to the mounted sample, and covered to facilitate the adsorption of the ethylene glycol. This treatment caused the basal spacing of the montmorillonite-type structures to expand to their characteristic spacing of 17 Å, enabling a positive identification of these minerals to be made. This technique is also useful for studying randomly interstratified illite-montmorillonite mixed layer clays (40). Heat treating the clays at 350°C makes it possible to estimate the amount of mixed layer clay content relative to the illite content (12). Figure 2 shows the shift of the 001 x-ray diffraction peak when clay minerals are glycolated and heated.

c. Quantification. After the identification of the mineral constitutents were made, x-ray diffraction was used to quantify the predominant minerals present. As mentioned before, the quantification of the mineral fraction was carried out by both a direct determination of a representative sample of the composite tails and by quantification and integration of each of the separate layeered fractions. The individual values obtained by the two methods were used to calculate a mean and a range for the minerals present.

The important minerals were quantified using the height of a characteristic x-ray diffraction peak of the particular mineral.

A set of standard curves relating peak height to mineral content (see Appendix A) was used to quantify the important minerals in the blackwater samples. This standard curve was prepared for each mineral by diluting a known standard mineral (see Table 8) with varying amounts of glass (amorphous to x-rays) and plotting the x-ray peak intensity versus the percentage of the standard mineral present. The relevant peak height of an unknown quantity of a mineral in a particular sample is then compared to this standard curve to determine the amount of mineral present. The standard curves for the dominant minerals are given in Appendix A.

Quantitative analysis was performed on powdered, dry-ground material that was mounted so as to obtain random orientation. This random orientation was achieved by mounting the powdered material into the hole of a donut-shaped metal mount somewhat similar to a washer. The mount was prepared by fastening one side of the ring to a glass slide using masking tape while the open side was used to fill the mount with the sample powder. Once the hole in the mount was filled, a button-type back was taped on. The ring and slide was flipped over, the glass slide was removed, and the sample holder placed, open side up, in the x-ray diffractometer, which rotates while the sample is being scanned. This type of mounting helps to achieve a random sample orientation which in turn produces a peak height that is not influenced by particle orientation to any great extent.

Table 8. Characteristic peaks used for quantitative analysis of the principal minerals found in blackwater.

Mineral	Peak Å (19)	Source of Standard Reference Sample
Illite	4.48, 2.57	API #34, Fithian, Illinois (Ward's)
Kaolinite	3.57	API #9 Mesa Alta, New Mexico (Ward's)
Chlorite	3.55	Calaveras Company, California (Ward's)
Calcite	3.04	Valentine, Center County, Pennsylvania
Quartz	1.82	Castastone Products Company, Inc. Raleigh, North Carolina
Dolomite	2.88	Thornwood, New York (Ward's)

Table 8 shows the characteristic peaks used for quantifying the predominant minerals. The peaks for kaolinite, chlorite, and calcite were chosen because of their strong intensity and relatively low interference from other minerals commonly found in coal. The 1.82 Å peak of quartz was used because the intensity of this peak at concentration of 10-20 percent was similar to the intensities of the peaks for the other minerals analyzed and therefore, the need to change the sensitivity of the recorder was less, thus producing more accurate results. The 4.48 Å and 2.57 Å peaks for illite were chosen after an x-ray scan was performed on the Fithian, Illinois, API #35, illite sample using a randomly oriented mount. Although these peaks are not the two most prominent illite peaks used in the slide identification scheme, they were found to be more satisfactory for random orientation quantification.

The "illitic" material—illite, interstratified illite-montmorillonite, and montmorillonite--were roughly quantified as a group since our ability to analyze this material was somewhat limited. X-ray diffraction and potassium analysis by atomic adsorption (23) were two methods used to quantify the illitic material. Problems associated with this quantification are discussed in Section IV.A.3.

When the only significant source of potassium in the mineral material is illite, then a determination of potassium content can be used as a means of quantifying the illitic clay if the stoichiometric amount of potassium in illite is known (5). Weaver (40) suggests a K_2O content of approximately 8.93 percent for most illites and a K_2O

content of 11.9 percent for mica. The K_2O content used for this analysis was 5.12 percent which is the K_2O content of the illite shale of Fithian, Illinois, after adjustment for contaminants. The amount of quartz and calcite in the illite standard was determined using the x-ray diffraction technique previously mentioned in this section. The percentage of K_2O in the standard was then adjusted to 100 percent illite, and this value was used to calculate the amount of illite present in the different samples based on their K_2O content. Atomic absorption was used to determine the amount of potassium oxide present in each sample (23). Greater details of this procedure are given in Appendix C.

C. Particle Size Characterization

1. Sample Preparation

Characterization of the particle size of blackwater involved the initial separation of the solids into a mineral fraction and a carbonaceous fraction using the froth flotation procedure outlined in Section III.B.1. Each of these fractions was then divided, by wet screening, at 400 mesh into a coarse and a fine fraction. The use of a wetting agent, Aerosol OT, improved the efficiency of this size separation. A drop, approximately 50 milligrams, of 75% Aerosol OT was applied to the screening surface of the sieve to help wet it, and another drop or two of the wetting agent was added to each fraction in order to wet the particles. The carbonaceous material tended to require more wetting agent than did the mineral matter, which would be expected since coal is naturally hydrophobic. The material was assumed to be wetted when skin flotation was not observed. The plus 400 mesh material of each fraction was drained, dried, and retained for further analysis. A 200 ml representative sample of the minus 400 mesh fraction was removed for analysis and the remaining slurry was filtered, dried, and weighed to determine the percent solids.

2. Sizing Method

The size distributions of the carbonaceous material and the mineral matter were determined separately. The plus 400 mesh fractions were screened using a Ro-Tap shaking device, and laboratory testing sieves (Tyler Standard Mesh). The minus 400 mesh fractions were analyzed using gravitational and centrifugal sedimentation methods. A Whitby Particle Size Analyzer, manufactured by Mine Safety Appliances (MSA) Company, Pittsburgh, Pennsylvania, and a Sedigraph, Model 5000 D, manufactured by Micromeritics Instrument Corporation, Norcross, Georgia, were used for subsieve particle analysis.

The MSA Particle Size Analyzer utilizes sedimentation, both gravity settling for the coarse particles and centrifugation for the fine, to determine particle size distribution (42). This method utilizes a special centrifuge tube with a small capillary at the bottom. The particle size distribution is calculated from the ratio of the observed sediment height in the capillary at times corresponding to the desired particle sizes; to the height after all particles have settled.

The Sedigraph employs a sedimentation method which uses an x-ray beam as a means of measuring the settling rate of particles (29). The application of the machine depends on the ability of the material being analyzed to absorb x-rays, which is related to the atomic number of the elements present in the material. Elements with low atomic numbers such as carbon, atomic number 6, do not absorb x-rays very well. Therefore, the Sedigraph could not be used to analyze the carbonaceous material, but was used to analyze the mineral matter since that material contained atoms of a high enough atomic number for adsorbance to occur.

The 200 ml sample of the minus 400 mesh material was concentrated by allowing the suspension to stand for a number of days so that all the material would settle, and the clear solution was decanted. Approximately 5-10 ml of the concentrated slurry was then transferred to a 35 ml bottle for dispersion treatment. The slurry was dispersed using an ultrasonic bath and bleach (Bransonic 12, Branson Cleaning Equipment, Shelton, Connecticut), about 50 ppm NaOCl, which was added to oxidize any organic flocculants present in the blackwater. A few drops of bleach were added to the 5-10 ml slurry and it was then placed in an Ultrasonic Bath for a half hour. The sample was then diluted to a total volume of approximately 25 ml using a stabilizing solution, and the sample was returned to the Ultrasonic Bath for another 15 minutes. The sample was then allowed to stand for an hour to determine the degree of dispersion. The degree of dispersion was also determined by the visual appearance of the material during the MSA analysis. If the material appeared not to be dispersed, then a few more drops of bleach were added to the slurry and it was subjected to additional ultrasonic treatment. The mineral matter which contained a large amount of clay was stablized using a 0.1 percent Calgon solution and sodium carbonate to adjust the pH to 8.5. The carbonaceous fraction was stabilized by the use of a few additional drops of bleach and distilled water. About 5 mg of Aerosol OT were added to the slurry to wet the material when it appeared to be sticking to the walls of the glass MSA tube during the size analysis.

D. Surface Properties of the Coal and Ash-Forming Minerals

The surface properties of the coal and ash-forming minerals were investigated using a Zeta Meter. The magnitude and sign of the charged surfaces of the blackwater constituents were determined as a function of pH in order to estimate the point of zero charge, PZC, for the different constituents.

The Zeta Meter, manufactured by Zeta Meter, Inc., New York, New York, was used to determine the electrophoretic mobility of coals and minerals as a function of hydronium ion concentration. Separate suspensions of coals and minerals were analyzed to determine their characteristic surface properties.

A dilute suspension of the material to be analyzed was placed in a tubular cell between two electrodes and a known voltage was applied across the ends of the cell. A microscope was used to determine velocity and direction of the particles. This information, together with the impressed potential, was used to determine the sign and electrophoretic mobility of the particles. The use of a microscope allows the operator to view the behavior of the individual particles, and this is especially helpful in determining if mineral species of different electrical properties are present.

IV. EXPERIMENTAL RESULTS AND DISCUSSION OF MINERALOGICAL CHARACTERIZATION

A. Identification and Quantification of the Solid Material Present in Blackwater

1. Introduction

The solid material in blackwater consists essentially of liberated mineral and carbonaceous matter. Because of the differences in the physical and chemical properties of the two different classes of material, it was necessary to analyze the materials separately. After the material had been separated by the flotation technique it was analyzed for the mineralogical content, particle size distribution, and surface properties of the solid material.

2. Carbonaceous Fraction

a. Introduction. The mineral matter and carbonaceous fractions from each blackwater sample were analyzed for ash and sulfur content using the procedure outlined in Section III.B.2. The total ash and sulfur content in each original sample was calculated from the ash and sulfur content of the fractions, determined experimentally, and the weights of these two fractions. Results of these analyses for the thirteen blackwater samples tested are shown in Table 9. The blackwater samples were separated into two groups--those from the Eastern and Western halves of the United States--because of differences in mineralogy due to geologic genesis. The 'Eastern' samples, those from the Appalachian or Mid-continent coal fields, were obtained from preparation plant thickener underflows or the feed to the slurry pond. The two Western samples, B.D. L Wa 12 and S.L.S. Ut 13, were obtained from a preparation plant slurry pond in the state of Washington and from the refuse conveyor from a plant in the state of Utah, respectively.

b. Eastern samples. The ash content of the eleven samples collected from coal preparation plants in the eastern half of the United States ranged from 20.4 to 70.3 percent, with an average of 41.0 percent. Most of the ash-forming mineral in these blackwater samples exist in a liberated form, and therefore the ash content of the carbonaceous fraction was reduced drastically by the flotation separation. The carbonaceous material has an ash content which ranges from 8.4 to 14.4 percent, with an average of 10.9 percent. At the same time, the percentage of ash in the mineral matter fraction averages 84.3 percent with a range of 70.5 to 88.2 percent. The ash content of the mineral matter will vary depending on the mineral composition since the ash content of mineral matter will not necessarily be equal to its original mass, but will generally be less than 100 percent . Upon heating to 750°C, minerals such as clays, carbonates, and pyrite will lose weight as they release water, carbon

Table 9. Percentage of ash and sulfur in blackwater samples.

Sample	Carbonaceous			Ash-Forming Minerals			Total	
	% Ash	% S	Wt %	% Ash	% S	Wt %	% Ash	% S
Eastern Samples								
Pi. W Pa 1	10.2	1.14	55.5	86.1	1.11	44.5	44.0	1.13
L.K. C Pa 2	9.2	1.75	64.2	79.3	2.36	35.8	34.3	1.97
L.K. C pa 3	11.9	1.06	66.0	81.8	1.46	34.0	35.7	1.20
L.F. C Pa 4	14.4	1.30	80.4	87.9	1.40	19.6	28.8	1.32
Po. M WVa 5	12.6	0.94	70.9	87.5	0.70	29.1	34.4	0.87
Po. W WVa 6	12.1	0.76	63.9	86.2	0.56	36.1	38.9	0.69
Pi./L.F. H Oh 7	10.9	2.26	84.1	70.5	5.23	15.9	20.4	2.73
E L Ky 8	10.8	0.71	47.9	87.1	0.56	52.1	50.6	0.63
Pr. J Ala 9	9.2	1.12	72.3	88.0	0.59	27.7	31.0	0.97
I6/5 J Ill 10	10.7	2.92	19.0	84.3	4.54	81.0	70.3	4.28
I6 W Ind 11	8.4	2.67	28.9	88.2	3.14	71.1	62.7	2.65
Average Eastern	10.9	1.51	59.4	84.3	1.97	40.6	41.0	1.68
Range Eastern	8.4- 14.4	0.71- 2.92	19.0- 84.1	70.5- 88.2	0.56- 5.23	15.9- 81.0	20.4- 70.3	0.63- 4.28

Table 9. Continued.

Sample	Carbonaceous			Ash-Forming Minerals			Total	
	% Ash	% S	Wt %	% Ash	% S	Wt %	% Ash	% S
Western Samples								
B.D. L Wa 12	42.5	1.30	27.2	79.5	0.42	72.8	69.4	0.66
S/L.S. Ut 13	21.8	1.14	50.1	71.2	1.22	49.9	46.5	1.18
Average Western	32.2	1.22	38.7	75.4	0.82	61.3	57.9	0.92
Range Western	21.8-42.5	1.14-1.30	27.2-50.1	71.2-79.5	0.42-1.22	49.9-72.8	46.5-69.4	0.66-1.18

dioxide, and sulfur dioxide, respectively, while the mass of quartz remains unchanged. Mineral matter that contains a high percentage of clays (60-70 percent), some carbonates and quartz (10-20 percent each), and a few percent of pyrite will have an ash content usually ranging between 80 and 90 percent. Excluding three samples which contained a small amount of carbonaceous material, Table 9 shows the average ash content of an essentially pure mineral matter fraction to be about 87 percent ash.

A microscopic examination was made of the mineral matter fraction from each sample separated by flotation to determine the amount of carbonaceous material, if any, that was not removed by the flotation step. The following samples were seen to contain a small amount of residual carbonaceous material:

	Wt %
L.K. C Pa 2	3 %
L.K. C Pa 3	5 %
Pi./L.F. H Oh 7	10 %

The mineral matter fraction of the remaining eight Eastern samples contained essentially no residual carbonaceous material. The low ash value for the mineral matter from sample Pi./L.F. H Oh 7 resulted from the presence of 10 percent carbonaceous material and 11 percent pyrite which undergoes substantial weight loss upon ashing. The carbonaceous material that was present in the mineral matter fraction of samples L.K. C Pa 2 and L.K. C Pa 3 consisted of large particles containing locked mineral and carbonaceous components. The difficulty in obtaining an efficient separation for these two samples may be due to the presence of some carbonaceous material of high ash content and large particle size. Sample Pi./L.F. H Oh 7 contained large carbonaceous particles, about 48 mesh, of relatively low ash content. The large particle size of this material and the possibility that the coal had become oxidized would make for a difficult flotation separation. Since the efficiency of the froth flotation separation method depends on the surface characteristics of the material, locking, and particle size, it is understandable why these three samples were not separated as efficiently as were the other eight.

The sulfur content of the Eastern samples ranged from 0.63 to 4.28 percent, with an average of 1.68 percent. The sulfur content of most of the mineral and carbonaceous fractions obtained by the flotation separation did not differ appreciably from that of the whole sample, and the sulfur content of the carbonaceous fraction ranged from 0.71 to 2.92 percent, with an average of 1.51 percent. A few of the samples, containing a significant amount of larger, liberated pyrite particles, showed a decrease in sulfur content of the carbonaceous material as compared to the total sample.

c. Western samples. The ash content of the two Western samples, B.D. L Wa 12 and S/L.S. Ut 13, as received, was 69.4 and 46.5 percent, respectively. The samples contained a carbonaceous material that was exceptionally difficult to separate from the mineral matter. Large amounts of fuel oil, about 10 lb/ton, were used during the froth flotation process to improve the floatability of the oxidized coal, but unfortunately, this also increased the floatability of the mineral matter as well. The separation process was further complicated by the presence of a small percentage of locked coal-gangue particles in Sample 12 and rather large locked particles in Sample 13. The efficiency of separation for these two samples was low as a result of these problems, and this inefficiency is indicated by the ash analysis of the carbonaceous material from these two samples. Microscopic examination of the mineral fraction of the samples shows that B.D. L Wa 12 contains 5 percent, and S/L.S. Ut 13 10 percent of carbonaceous material. Sample 13 also contains a large quantity of carbonate minerals which have a high weight loss due to the release of carbon dioxide on ashing, and this would produce a lower percentage of ash for the mineral matter fraction. The sulfur content of S/L.S. Ut 13 was low and, as with the Eastern samples, was relatively constant between the carbonaceous and mineral matter fractions, while B.D. L Wa 12 contains mineral matter that is much lower in sulfur than the carbonaceous material.

d. Summary. Quantification of pyrite and/or marcasite in the mineral fraction was determined by a chemical method which is discussed in the section on sulfur analysis. The amount of sulfur in the mineral fraction was accredited as pyrite since this was the most common form of sulfur identified in the mineral fraction. No gypsum was detected by x-ray diffraction analysis though some may have been present in quantities below the detection limit of the x-ray method (a few percent). One percent of gypsum contained in a mineral matter sample would produce 0.19 percent sulfur in the overall sulfur analysis. Since the sulfur content of the mineral matter was greater than 0.42 percent for all of the samples and was usually greater than 1.0 percent, if any significant portion of this sulfur were due to gypsum, the gypsum content would be great enough to be readily identified by x-ray methods. In this way, absence of all but a percent or two of gypsum is confirmed.

Overall, the quality of the carbonaceous fraction was close to that expected of a clean coal product from the various mines with the exception of samples B.D. L Wa 12 and S/L.S. Ut 13. The sulfur and ash content of the various carbonaceous fractions was slightly high if the material is considered to be the only component of a high quality, clean coal product, but is sufficiently low for the material to be blended with the normal, coarser clean coal product without lowering the quality of the total product significantly. The largest difference between the quality of the carbonaceous material and that of the total sample was in ash content. Furthermore, it must be remembered that the blackwater from several of these plants had already passed through a flotation circuit so the easy-to-float, low ash fraction had already been removed ahead of the thickener or slurry pond.

In spite of the shortcomings of the flotation process, the ash content of the carbonaceous material was reduced drastically.

For most of the samples the ash content decreased by an average of 73 percent. The change of sulfur content of the carbonaceous material from that of the original solids contained in the blackwater samples was slight in most cases, some carbonaceous material decreased while others increased slightly in sulfur content.

This effective use of flotation to remove coal from the blackwater, and the relatively high percentages of carbonaceous material contained in the as-received blackwater samples (59.4 percent average, by weight of the Eastern samples and 38.7 percent average, by weight for the Western samples) indicate the advantage of an increased use of the flotation process to remove additional clean coal from current blackwater discharge streams. Not only would this result in an increased production of clean coal but would also lower the loading on the water clarification and recycle circuit, and increase the expected life of the fine refuse disposal area.

The difference in carbonaceous material content for the thirteen blackwater samples was more than likely due to a difference in mining and preparation methods employed at the different mines rather than to a difference in the type of coal being mined. Some of the samples were obtained from surface mines, though most of the samples were from underground mines. The complexity of the preparation plants varied widely, with some plants treating only the coarse coal while others cleaned both coarse and fine.

3. Ash-Forming Mineral Matter

a. Introduction. The ash-forming mineral matter (hereafter simply called "mineral matter") in each sample was identified and quantified using the x-ray diffraction procedure outlined in Section III.B.3. An exception was the determination of the amount of pyrite present, which was determined by the chemical method discussed in Section III.B.2c. Because of mineralogical differences in the solid material resulting from differences in geologic genesis, the blackwater samples were separated into two distinct groups, Eastern and Western.

The following minerals found in the blackwater samples were quantified using the x-ray diffraction procedure previously mentioned: kaolinite, chlorite, calcite, quartz, and dolomite. The mineral content of each sample was determined by comparing the height of the characteristic x-ray diffraction peak(s) of a given mineral to a standard curve of peak height *versus* percent of a particular mineral present.

For the "illitic" minerals--illite, montmorillonite, and interstratified illite-montmorillonite--this procedure was not uniformly successful because of structural irregularities and a modified technique had to be adopted. Some of the main types of structural irregularities which occur in these clay types are (22):

1. Random piling of layers.

2. Bending of layers.

3. Variation of composition within the layers.

4. Variation of composition from layer to layer.

Structural irregularities in these clays may be determined from their x-ray diffraction pattern. Random piling of layers of illite with montmorillonite is determined by the shape of the 10 Å peak (12,22) by mounting the clay on a glass slide and treating it with ethylene glycol to expand the layers from 9 Å to 17 Å. The glycolated clay is then scanned by x-ray diffraction to identify this expansion. An interstratified illite-montmorillonite clay is identified by the skewed shape of the 10 Å peak, and the amount of broadening of the 10 Å peak on the low angle side is used to estimate the degree of interstratification of the illite-montmorillonite. Well-crystallized mica can be distinguished from the "illitic" material by the presence of a sharp, narrow peak at 10 Å (33).

b. Eastern samples. The mineral matter in the eleven black-water samples obtained from operatons in the Midwestern and Appalachian coal fields was found to be similar. This is not unexpected since they all date from the Pennsylvanian Period. Each sample contained a large amount of "illitic" material, with most of the samples containing lesser amounts of kaolinite, chlorite, calcite, quartz, and pyrite. The illitic material in each sample was characterized by these methods:

a. Identification of the type of illitic clays present.

b. Description of the shape of the 10 Å peak.

c. Identification of the dominant, 15% or greater, illitic clays.

Using this system the following results were obtained for each sample:

Pi. W Pa 1

a. Illite, interstratified illite-montmorillonite, montmorillonite.

b. Very broad at the low angle side.

c. Moderately interstratified illite-montmorillonite.

L.K. C Pa 2

a. Illite, interstratified illite-montmorillonite, montmorillonite.

b. Slightly broad at the low angle side.

c. Illite, slightly interstratified illite-montmorillonite.

L.K. C Pa 3

a. Illite, interstratified illite-montmorillonite, montmorillonite.

b. Very slight broadening at the low angle side.

c. Illite.

L.F. C Pa 4

a. Illite, interstratified illite-montmorillonite, montmorillonite.

b. Very broad peak at the low angle side.

c. Highly interstratified illite-montmorillonite.

Po. M WVa5

a. Illite, muscovite.

b. Very sharp peak with no broadening at the low angle side.

c. Illite.

Po. W WVa 6

a. Illite, interstratified illite-montmorillonite, montmorillonite, muscovite.

b. Sharp peak with some broadening at the low angle side.

c. Illite.

Pi./L.P. H Oh 7

a. Illite, interstratified illite-montmorillonite, montmorillonite, hydromuscovite.

b. Broad peak at the low angle side.

c. Moderately stratified illite-montmorillonite.

E L Ky 8

a. Illite, interstratified illite-montmorillonite, montmorillonite, muscovite.

b. Slight broadening of the low angle side.

c. Illite.

Pr. J Ala 9

a. Illite, interstratified illite-montmorillonite, montmorillonite, muscovite.

b. Slight broadening at the low angle side.

c. Illite.

I6/5 J 111 10

a. Illite, interstratified illite-montmorillonite, muscovite.

b. Very broad at the low angle side.

c. Highly interstratified illite-montmorillonite.

I6 W Ind 11

a. Illite, interstratified illite-montmorillonite, montmorillonite, muscovite.

b. Very broad at the bottom half of the peak at the low angle side.

c. Illite, highly interstratified illite-montmorillonite.

The type of "illitic" material present in these samples was sometimes seen to vary substantially in crystallinity. For example, sample L.F. C Pa 4 contains an illitic material of poor crystallinity composed of a highly interstratified illite-montmorillonite with significant amounts of illite and montmorillinite present, while sample Po. M WVa 5 contained an illitic material, of good crystallinity, composed mainly of illite and some muscovite. The samples studied from West Virginia, Kentucky, and Alabama contained an "illitic" material of relatively good crystallinity with very little or no interstratification of montmorillonite with the illite, while the samples from Pennsylvania, Ohio, Indiana, and Illinois contained an illitic material of varying crystallinity and interstratification.

Quantifying the illitic material by x-ray diffraction using peak height has many limitations, and the structural irregularities in illitic clays limits the use of x-ray diffraction as a means of quantifying these clay minerals. Because of these difficulties in quantification, three different methods were used in order to estimate the percentage of illite present.

Method 1, Direct X-Ray Quantification

X-ray diffraction was used to quantify the illitic material directly. The peak heights at 4.48 Å and the 2.57 Å were used for quantification. A standard curve was prepared by diluting a known standard illitic clay (Fithian, Illinois, APL #35) with varying amounts of glass and plotting the x-ray peak intensity *versus* the percentage of the standard illite present. The height of the relevant peak of an unknown is then compared to this standard curve to determine the amount of illite present.

Method 2, Potassium Analysis

Assuming that illite is the only mineral present containing a significant percentage of potassium and, furthermore, that the potassium content of all of the illitic material studied remains essentially constant, the amount of illite present in a given sample may be approximated by comparing the percentage of K_2O present in a given sample to the K_2O content in a standard sample (in this case: Fithian, Illinois shale, Appendix C).

Method 3, Difference Method

The difference method consisted of quantifying the amount of all of the other minerals present (kaolinite, chlorite, calcite, quartz, and pyrite) and crediting the balance of the mineral matter, not previously quantified, to the illitic group of minerals.

The results of the illitic clay mineral analysis by the three methods are shown in Table 10. The "best" value was usually an average of the direct and difference methods, though in four cases the K_2O method was also used in arriving at the "best" value. In the one case where the mineralogical analysis as determined by direct x-ray quantification did not total near 100 percent, the value obtained by the difference method was assumed to be more accurate than the other two methods. This is a reasonable assumption because the difference values are not influenced by the structural irregularities of the illitic material. The difference average was obtained by averaging the two difference values obtained by analyzing the mineral matter that was separated into layers using the centrifuging technique discussed in Section III.B.3. and by analyzing a representative sample of the composite mineral matter. The potassium analysis generally produced values that were not in complete agreement with the other two methods, but the method served as a guide. The reason for the poor agreement of the potassium results may be due to the large variation in the amount of montmorillonite and mica present in the different blackwater samples.

Four samples (Nos. 7, 9, 10, and 11) show fairly good agreement using all three methods, while all but one of the samples (L.F. C Pa 4) show reasonable agreement between the difference method and the direct x-ray method. The poor agreement for this sample was due to the presence of a large amount of highly interstratified illite-montmorillonite and its poor crystallinity. For

Table 10. Approximate illitic[a] mineral content in the mineral matter fraction from eastern blackwater samples.

Thickener Underflow Sample	(1) Based on Direct X-ray Quantification	(2) Based on K_2O Analysis	(3) Based on Difference Method Average	"Best" Value	Source of "Best" Value Technique
Weight Percent					
Pi. W Pa 1	48	37	51	50	1,3
L.K. C Pa 2[b]	45	34	50	48	1,3
L.K. C Pa 3[b]	48	34	53	51	1,3
L.F. C Pa 4	26	39	59	59	3
Po. M WVa 5	53	71	59	56	1,3
Po. W WVa 6	45	68	50	48	1,3
Pi./L.F. H Oh 7[b]	43	37	45	42	1,2,3
E L Ky 8	55	80	69	62	1,3
Pr. J Ala 9	56	67	70	64	1,2,3
I6/5 J 111 10	48	47	44	46	1,2,3
I6 W Ind 11	60	60	48	56	1,2,3

Table 10. Continued.

Thickener Underflow Sample	(1) Based on Direct X-ray Quantification	(2) Based on K_2O Analysis	(3) Based on Difference Method Average	"Best" Value	Source of "Best" Value Technique
Weight Percent					
Average	48	52	54	53	
Range	26-60	34-80	45-70	46-64	

---

[a] Illitic material: Illite, interstratified illite-montmorillonite, montmorillonite, clays.
[b] Values have been adjusted for carbonaceous content.

those samples showing general agreement between these two methods, the largest difference between methods is only 14 percent (Samples E L Ky 8, Pr. J Ala 9) while 6 of the 11 samples show a difference of 5 percent or less. Differences in structural irregularities in the illitic minerals contained in these samples undoubtedly was the cause of the variation between the three methods of analysis.

A summary of the mineral matter content of all these Eastern blackwater samples is given in Table 11. Illitic material is seen to be the dominant constituent in each sample tested, together with varying and lesser amounts of quartz, calcite, and kaolinite, and much smaller amounts of chlorite and pyrite. These minerals accounted for essentially all of the mineral matter present in most of the samples, though some samples also showed small amounts of dolomite, feldspar, rutile, and siderite. These minor minerals are also shown in Table 11.

Because of the method used to obtain, especially, the "best" value for illitic material, the mineral composition of each sample does not necessarily total exactly 100% but range from 94 to 106.

A comparison of data from the O'Gorman and Walker study on the mineral constitutents in coal (27) with the data from the present study on the mineral constituents in the blackwater effluent from coal preparation plants was made. Table 12 shows the results of O'Gorman and Walker's analytical results for some of the same coal seams as were examined in the present study. As may be seen from Table 12, the dominant mineral in most of these coals is kaolinite, together

Table 11. Approximate composition of the mineral matter fraction from eastern blackwater samples (weight percent).

Sample	Illitic Material				Kaolinite		Quartz		Calcite		Chlorite		Pyrite	Other Minerals
	"Best"[a] Value	Illite	Illite-Mont.	Mont.	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range		
Pi. W Pa 1	50	sig.	dom.	sig.	12	10-14	18	14-21	19	18-20	3	2-3	2	
L.K. C Pa 2[b]	48	dom.	dom.	sig.	17	15-19	14	11-16	12	11-13	4	3-4	4	R
L.K. C Pa 3[b]	51	dom.	sig.	sig.	22	20-23	9	6-11	14	12-16	4	3-5	3	
L.F. C Pa 4	59	sig.	sig.	sig.	7	3- 8	8	7- 9	21	19-23	3	2-3	3	
Po. N WVa 5	56	dom.	sig.	---	11	9-13	17	16-18	6	5- 7	6	6-6	1	D, R, S
Po. W WVa 6	48	dom.	sig.	sig.	15	13-17	15	14-16	17	15-18	5	3-6	1	R, S
Pi./L.F. N Oh 7[b]	42	sig.	dom.	sig.	8	7- 8	16	13-19	13	12-14	3	2-3	11	R
E L Ky 8	62	dom.	sig.	sig.	8	6 -9	13	12-14	0	---	7	6-7	1	F, R, S
Pr. J Ala 9	64	dom.	sig.	sig.	7	6- 7	14	13-14	0	---	4	3-5	1	D
I6/5 J Ill 10	46	sig.	dom.	---	6	3- 8	21	19-22	22	17-26	0	---	9	
I6 W Ind 11	56	dom.	dom.	sig.	14	10-17	22	21-22	4	1- 7	4	3-5	6	
Average	53				11		15		12		4		4	
Range of Average	46-64				6-22		8-22		0-22		0- 7		1-11	

[a] From Table 10.
[b] Values have been adjusted for carbonaceous content.

Significant: 5-15%
Dominate: Greater than 15%
D--Dolomite; F--Feldspar; R--Rutile; S--Siderite

Table 12. Approximate mineral matter composition in U.S. coal seams (weight percent). (modified after O'Gorman and Walker)(27)

PSOC Sample Number	Seam	Locality	Kaol.	Ill.	Mus.	Chl.	Mont.	Mix.	Cal.	Dol.	Qtz.	Gyp.	Pyr.
Eastern Samples													
2	#3 Elkhorn	Deane, Ky.	40-50	trace	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	30-40	1-10	1-10
3	#3 Elkhorn	Deane, Ky.	30-40	trace	n.d.	trace	n.d.	trace	n.d.	n.d.	40-50	1-10	1-10
4	#3 Elkhorn	Deane, Ky.	1-10	1-10	n.d.	1-10	trace	1-10	n.d.	n.d.	1-10	10-20	10-20
6	#3 Elkhorn	Deane, Ky.	40-50	1-10	n.d.	1-10	n.d.	n.d.	n.d.	n.d.	10-20	1-10	1-10
22	#6 Illinois	Victoria, Ill.	20-30	10-20	n.d.	trace	n.d.	1-10	n.d.	n.d.	10-20	1-10	10-20
26	#6 Illinois	Carrier Mills. Ill.	trace	1-10	n.d.	1-10	trace	1-10	n.d.	n.d.	1-10	1-10	60-70
103	Pittsburgh	Washington Co., Pa.	50-60	10-20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10-20	1-10	1-10
103A	Pittsburgh	Washington Co., Pa	>70	1-10	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	1-10	1-10	1-10
108	Pittsburgh	Marianna, Pa.	20-30	1-10	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	1-10	n.d.	30-40
109	Pittsburgh	Marianna, Pa.	30-40	10-20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10-20	10-20	1-10
110	Pittsburgh	Marianna, Pa.	40-50	10-20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1-10	trace	20-30
111	Pittsburgh	Marianna, Pa.	30-40	30-40	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	10-20	1-10	10-20
113	Lr. Kittanning	Tire Hill, Pa.	40-50	1-10	n.d.	n.d.	n.d.	1-10	trace	n.d.	1-10	1-10	30-40
114	Lr. Kittanning	Tire Hill, Pa.	50-60	10-20	n.d.	trace	n.d.	1-10	n.d.	n.d.	10-20	1-10	trace
116	Lr. Freeport	Ehrenfeld, Pa.	30-40	1-10	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	1-10	1-10	30-40
125	Lr. Freeport	Hastings, Pa.	30-40	10-20	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	10-20	1-10	10-20
126	Lr. Kittanning	Ebensburg, Pa.	50-60	n.d.	n.d.	n.d.	n.d.	1-10	trace	n.d.	1-10	1-10	10-20
127	Lr. Kittanning	Ebensburg, Pa.	60-70	10-20	n.d.	n.d.	n.d.	1-10	1-10	n.d.	1-10	1-10	1-10

Table 12. Continued.

PSOC Sample Number	Seam	Locality	Kaol.	Ill.	Mus.	Chl.	Mont.	Mix.	Cal.	Dol.	Qtz.	Gyp.	Pyr.
128	Lr. Kittanning	Ebensburg, Pa.	50-60	1-10	n.d.	n.d.	n.d.	1-10	trace	n.d.	1-10	trace	20-30
129	Lr. Kittanning	Ebensburg, Pa.	>70	n.d.	n.d.	n.d.	n.d.	1-10	1-10	n.d.	1-10	1-10	1-10
132	Pocahontas #3	Gary, W.Va.	10-20	n.d.	n.d.	1-10	n.d.	trace	trace	10-20	10-20	10-20	1-10
133	Pocahontas #3	Gary, W.Va.	30-40	n.d.	n.d.	1-10	n.d.	1-10	1-10	n.d.	1-10	10-20	trace
135	Pratt	Hueytown, Ala.	50-60	10-20	10-20	trace	n.d.	n.d.	n.d.	n.d.	10-20	1-10	1-10
136	Pratt	Hueytown, Ala.	60-70	1-10	1-10	n.d.	n.d.	n.d.	n.d.	n.d.	1-10	1-10	1-10
137	Pratt	Hueytown, Ala.	20-30	n.d.	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	1-10	1-10	50-60
Western Samples													
67	Lower Sunnyside	Horse Canyon, Ut.	10-20	1-10	n.d.	n.d.	n.d.	1-10	n.d.	n.d.	1-10	20-30	20-30

Kaol.--Kaolinite
Ill.--Illite
Mus.--Muscovite
Chl.--Chlorite
Mont.--Montmorillonite
Mix.--Mixed Layered Illite-Montmorillonite
Cal.--Calcite
Dol.--Dolomite
Qtz.--Quartz
Gyp.--Gypsum
Pry.--Pyrite
Trace = < 1.0%
n.d. = not detected

with lesser amounts of illite, interstratified (mixed layer) illite-montmorillonite, quartz, gypsum, and pyrite. It is worth noting that chlorite and calcite were not usually detected in their study.

Table 11 and 12 show that the commonly reported minerals in both studies were kaolinite, illite, interstratified illite-montmorillonite, quartz, and pyrite. Thus, although both studies indicate the presence of the same types of minerals, the quantity of some of them is strikingly different. O'Gorman and Walker show kaolinite to be the dominant mineral in most of their samples, while this study consistently shows the illitic material to be dominant. The two studies also disagree sharply in the type of minerals that show up in lesser amounts. Table 12 shows gypsum to be a mineral commonly found in the coal samples studied by O'Gorman and Walker, while chlorite and calcite were rarely found in their samples. In contrast to this, Table 11 shows that chlorite and calcite were common in most of the blackwater samples studied, while gypsum was not detected in any of the samples. The differences in mineral composition found in the two studies strongly indicate that the composition of the mineral matter contained in the blackwater was influenced by some source other than the minerals inherent in the coal seam.

The high illitic clay content in the blackwater samples indicates that a large amount of the mineral material in the blackwater is of a shale origin. It is well known that the clay fraction of most Pennsylvanian shales contains a large illitic clay fraction, $\sim$80 percent (40), together with $\sim$17 percent kaolinite and $\sim$3 percent chlorite. Some of the other minerals commonly found in shales are quartz and carbonates. The clay content of shales, in general, is usually about 60 percent, with illite the most abundant clay mineral, montmorillonite and mixed-layer illite-montmorillonite next, followed by kaolinite, chlorite, and mixed-layer chlorite-montmorillonite (40). Other clay minerals are relatively rare in normal sediments (40). Furthermore, the presence of chlorite in all but one of the Eastern blackwaters reinforces the conclusion as to the presence of shale constituents material in the blackwater. Chlorite is commonly found in roof shales of Pennsylvania coals but is rarely found within the coal seam (12).

Most run-of-mine coal contains roof and floor material that has become mixed with the coal during the mining operations, and it is common for run-of-mine coal to have an ash content of 15 percent or greater. This ash content may go as high as 40 percent for some operations. Since this is substantially higher than the 5-10 percent ash inherent in a coal seam, the balance of the ash must come from overbreak during the mining operation. As an ever greater amount of mechanization is introduced, such as the continuous miner and the longwall, such overbreak material from floor and/or roof may be expected in all run-of-mine coal in increasing amounts. Since part of this shaley material is quite soft, and would decompose easily during processing, its presence in the blackwater effluent from a coal preparation plant is virtually assured.

The composition of the mineral material in the eleven thickener underflow blackwater samples thus bear a much more striking similarity to the composition of the Pennsylvanian shales than to the mineral composition of Pennsylvanian coals. Hence, the mineral composition of the coal appears to have little influence on the composition of the mineral matter in the blackwater, but is largely determined by the nature of the adjacent roof and floor horizons which are introduced into the run-of-mine coal by overbreak during the mining operation.

c. Western samples. Two samples of waste material from coal operations in the western part of the United States were also tested. The mineralogical composition of these two samples is very different from that of the other samples, and therefore is discussed separately.

Sample B.D. L Wa 12 was obtained from a slurry pond of an operation in Washington state. Because the sample was obtained from a settling pond rather than from a thickener underflow, as was true for most of the other samples, the mineral matter may be expected to be substantially finer in particle size than that of the other samples. The sample was analyzed in the same manner as were the other samples, except that the lack of illite as a major constituent allowed quantification to be made using x-ray diffraction analysis alone. The separated mineral matter fraction from flotation was concentrated into layers by centrifuging the slurry and removing each layer separately for quantification.

Identification of the major minerals in each layer was determined using the x-ray diffraction procedure outlined previously, Section III.B.3. The mineral matter in this sample was found to consist of a large clay fraction, mainly a montmorillonite, together with plagioclase feldspars. The mineral material in the top layer which consisted exclusively of the finest particles, was found to be mostly montmorillonite. Thus, this layer was used as a standard to estimate the amount of montmorillonite in the other layers and in the total sample. Since no other minerals were found, and because of the prominence of the characteristic x-ray diffraction peaks for feldspar, the balance of the material was accredited to feldspar. The presence of about 5 percent coal in the mineral matter was quantified by microscopic examination and corrected from volume to weight percent using the appropriate density.

The mineral composition of this sample is thus substantially different from the other twelve samples in that this sample contained a large amount of feldspar minerals. Montmorillonite was the only clay constituent detected in the sample, which is also unusual.

Approximate Mineral Composition of Sample B.D. L Wa 12

Mineral	Percentage
Montmorillonite	70
Feldspar	30

Sample S/L.S. Ut 13 was a refuse sample obtained from a coal preparation plant in Utah that treats coal mined in both Utah and Colorado. Mineral analyses were performed on the minus 28 mesh material obtained by screening the coarse refuse product.

The sample was separated into carbonaceous and mineral fractions using the same froth flotation procedure as was used with the other samples. The mineral fraction was then split at 400 mesh and the coarse and fine fractions were analyzed separately using x-ray diffraction. The minerals present in this sample were similar to those found in the Pennsylvanian samples except for both a higher dolomite content and a higher montmorillonite content. The montmorillonite was identified using the oriented mount technique described in Section III.B.3. and quantified by the difference method.

Approximate Mineral Composition of Sample S/L.S. Ut 13

Mineral	Percentage
Montmorillonite	31
Kaolinite	24
Quartz	12
Calcite	17
Dolomite	14
Feldspar	< 1
Pyrite	2

As may be seen from Table 12, the mineral matter inherent in the Lower Sunnyside seam contains about 20-30 percent gypsum, whereas no gypsum was detected in the refuse material from the coal preparation plant treating coal from the Lower Sunnyside seam. The lack of gypsum in the refuse sample suggests the possibility that the mineral composition of the refuse had been influenced by some source other than the coal itself. Again, the most likely source of this mineral matter is the material bordering the coal seam. The fact that the coal fed to this plant is produced by underground mining, where overbreak is much more difficult to control than in surface mining, supports the idea that the bordering material has a major influence on the mineral composition of the refuse. Other possibilities may be variation of mineral composition within the mining area, or that coal from the Lower Sunnyside seam was not being treated at the time this refuse sample was taken. The high clay content of this sample was similar to that of the Eastern samples, although the high montmorillonite content of this sample is certainly not like the Pennsylvanian samples, but is more typical of the other Western sample.

Summary Samples B.D. L Wa 12 and S/L.S. Ut 13 were from Western coal seams that belong to the Tertiary and Cretaceous geological periods, respectively, while the eleven Eastern samples, discussed previously, belong to the Pennsylvanian period. The mineral composition of the two Western samples differs from the other eleven samples in that the Western samples contain a significant amount of montmorillonite clay and essentially no illite clay. Sample S/L.S. Ut 13 contains some of the typical minerals found in the Eastern, or Pennsylvanian period, samples such as kaolinite, quartz, and calcite. Again, the mineralogical composition of the mineral matter from these two samples was probably determined by the mineralogical nature of the adjacent strata.

d. Summary. It appears that the composition of the mineral matter in the effluent from a coal preparation plant will more than likely resemble the mineral composition of the adjacent strata rather than the mineral composition inherent in the coal seam itself. The evidence for this is especially strong since the mineralogical composition of the samples, and most especially the high illite content, is much more characteristic of the adjacent Pennsylvanian shales than of the mineral matter inherent in the coal seam. The amount of clay in the blackwater of a coal preparation plant may be an indication of the degree of difficulty expected when treating a "blackwater." Clay minerals consist of very small platelet-shaped particles often with a mean size of a few micrometers or smaller. Because of their very slow settling rate, these particles in a blackwater can be expensive and difficult to remove. Montmorillonite clays, such as those found in the two Western samples, are often even more difficult to flocculate efficiently and higher turbidities in the recycled water are to be expected.

B. Particle Size Analysis

1. Evaluation of Sizing Methods

Each blackwater sample after being separated into carbonaceous and mineral fractions by flotation, was then split at 400 mesh. The coarse fraction was analyzed using sieving techniques and the fine fraction was analyzed using the MSA Whitby Particle Size Analyzer. A comparison of some subsieve results was made between those of the MSA Whitby Analyzer with those obtained from the Sedigraph, manufactured by Micromeritics Instrument Corporation, Norcross, Georgia.

A comparison between these two instruments was made to determine the reliability of the MSA results. Allen (1) points out some of the disadvantages of the MSA apparatus. These include: possible compression of the sediment column with increasing speed during centrifuging; the glass tube is the wrong shape to prevent wall effects during settling; hindered settling in the neck of the capillary eliminating the analysis of materials with a narrow size range, which will settle at about the same time; and the loss of sedimentation height as material builds up in the capillary. However, the results noted in this study are so reproducible that these effects are probably not of major importance. The main advantage of the method is that it is suited to both the gravitational and centrifugal range, hence, a size range from about 0.2 to 80 μm may be analyzed. In this particular study the MSA was especially suitable since it offered a relatively fast method of analysis for both the mineral and the carbonaceous sub-sieve fractions.

Figures 3 and 4 show the results obtained when the mineral fractions of two of the thirteen samples were analyzed by these two different methods. The results of both analyses agree relatively well, especially above 1 μm. This agreement indicates that the sub-sieve analysis performed with the MSA Whitby Particle Size Analyzer is quite reliable. The carbonaceous material in blackwater made the Sedigraph impractical for the analysis of both the mineral and the carbonaceous fractions and therefore, it was not used as the main method of sub-sieve size analysis.

Two MSA analyses were used to determine the sub-sieve size distribution of the minus 400 material in each sample. The values of the two tests were plotted on Rosin-Rammler paper, and a smooth curve was drawn through the points to produce the sub-sieve size distribution for that particular sample. The values of the sub-sieve size distribution were then combined with the sieve analysis by multiplying the sub-sieve values by the value for the fraction of material in that particular sample that was finer than 400 mesh. There appeared to be no need to use a shape factor to incorporate the sieve and sub-sieve results since most of the results produced a relatively smooth curve. The size analysis data of the sieve and sub-sieve material for the thirteen blackwater samples is in Appendix D.

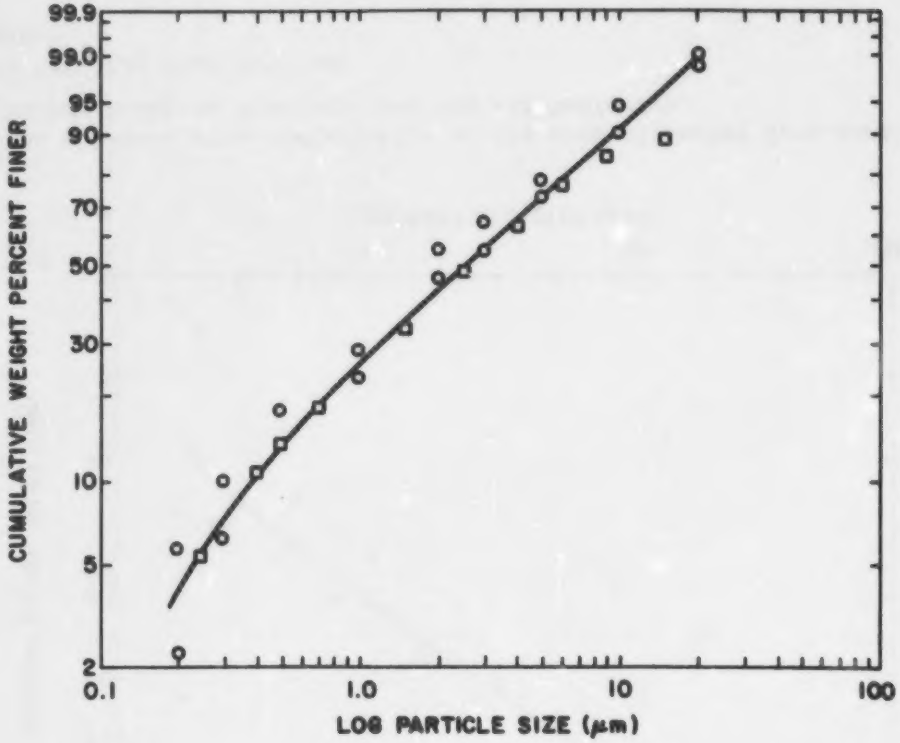

Figure 3. Comparison of subsieve size distribution of the mineral matter from sample E L Ky 8 using the Whitby Particle Size Analyzer and the Sedigraph.

○ Whitby Particle Size Analyzer
□ Sedigraph

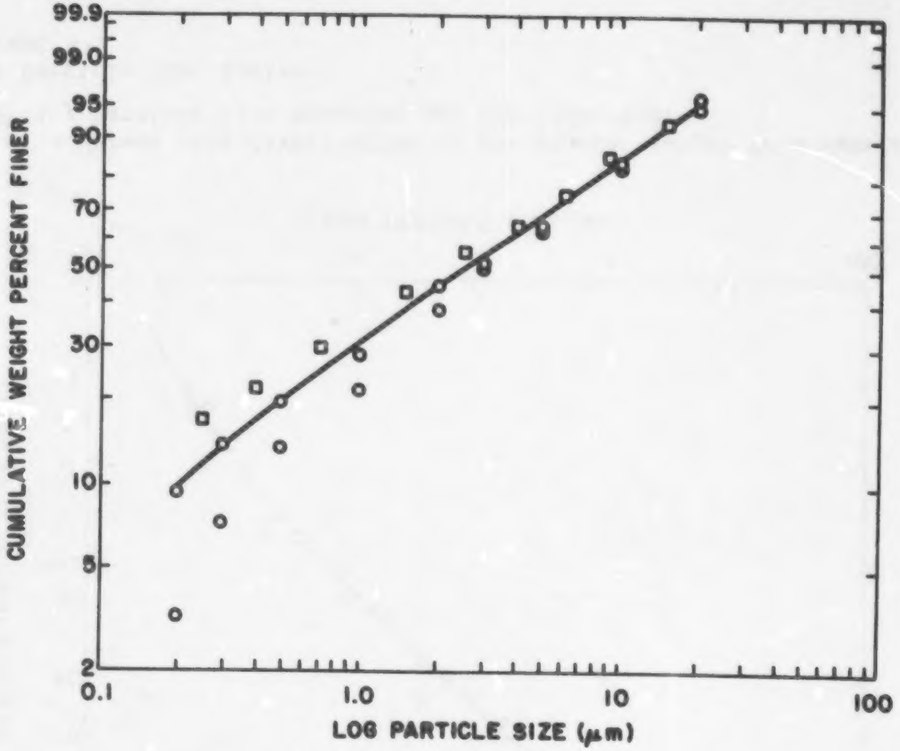

Figure 4. Comparison of subsieve size distribution of the mineral matter from sample S/L.S. Ut 13 using the Whitby Particle Size Analyzer and the Sedigraph.

○ Whitby Particle Size Analyzer
□ Sedigraph

2. Particle Size Distribution of Blackwater Solids

Size distributions for all thirteen samples are shown in Figures 5 through 13. The size distribution of the mineral fraction was significantly finer than that of the carbonaceous fraction for each sample analyzed. The difference in size distribution between the two fractions is presumably due to the high clay content in the mineral fraction. Clay minerals have layer structures with very weak bonding between layers (14). Since water can penetrate between the layers, the particles readily break down in suspension and their size tends to be somewhat limited. X-ray diffraction results show an extremely high clay content in the mineral matter, especially in the finer material.

In addition to differences in relative fineness, the distributions for the coal and mineral fractions have quite different shapes. The shape of the distribution curves for the mineral material of the different samples are similar and somewhat unusual. The mineral distribution curves have a flat portion starting at about 74 μm and ending at about 20 μm, indicating the presence of very few particles within that range. This plateau is a result of a decrease in the amount of "coarse minerals" such as quartz, calcite, and pyrite at about 74 μm and an increase in the clay minerals at about 20 μm or less. To verify that this plateau was real and not simply an artifact of the measurement technique, additional sedimentation analyses were carried out. In these tests, MSA determinations were made on the minus 200 mesh (74 μm), mineral matter rather than on the minus

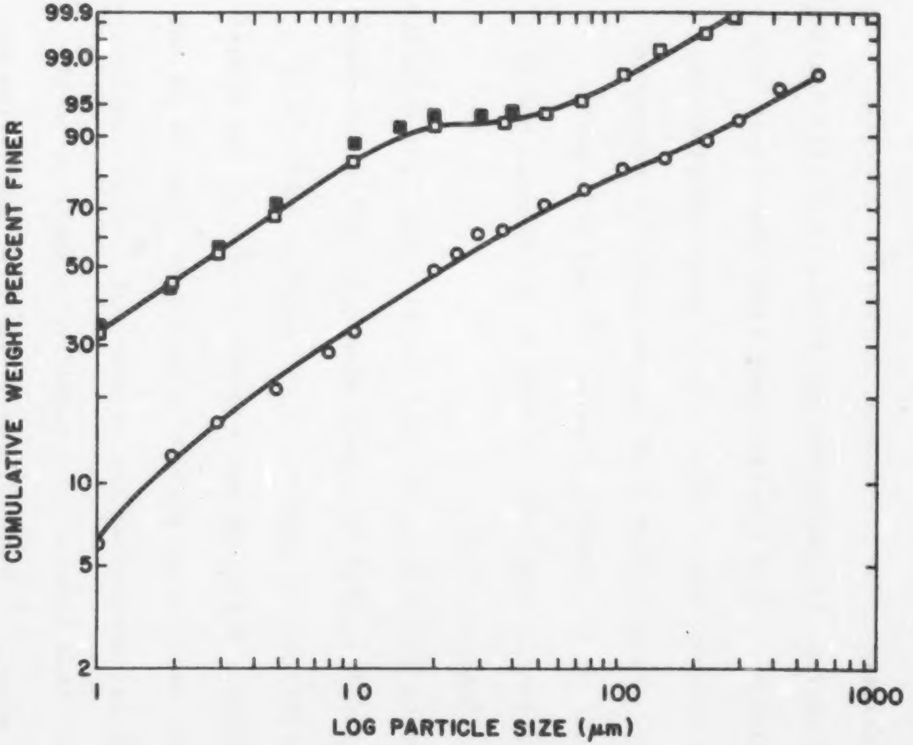

Figure 5. Particle size distribution of blackwater solids, sample no. Pi W Pa 1. (Pittsburgh Seam, Washington County, Pennsylvania, 55.5 Wt % Coal)

○ Carbonaceous
☐ Mineral matter MSA used for minus 37 μm
■ Mineral matter MSA used for minus 74 μm

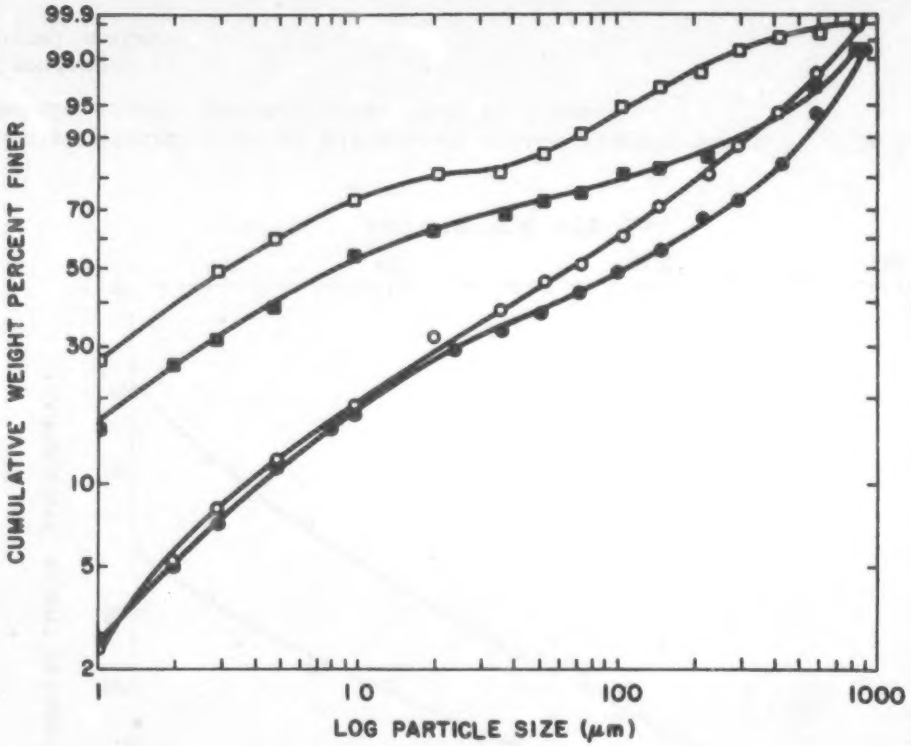

Figure 6. Particle size distribution of blackwater solids from the Lower Kittanning samples, sample no. L.K. C Pa 2 and L.K. C Pa 3. (L.K. C Pa 2--Lower Kittanning Seam, Cambria County, Pennsylvania, 64.2 Wt % coal; L.K. C Pa 3--Lower Kittanning Seam, Cambria County, Pennsylvania, 66.0 Wt % coal)

Sample No. L.K. C Pa 2
○ Carbonaceous
□ Mineral matter

Sample No. L.K. C Pa 3
● Carbonaceous
■ Mineral matter

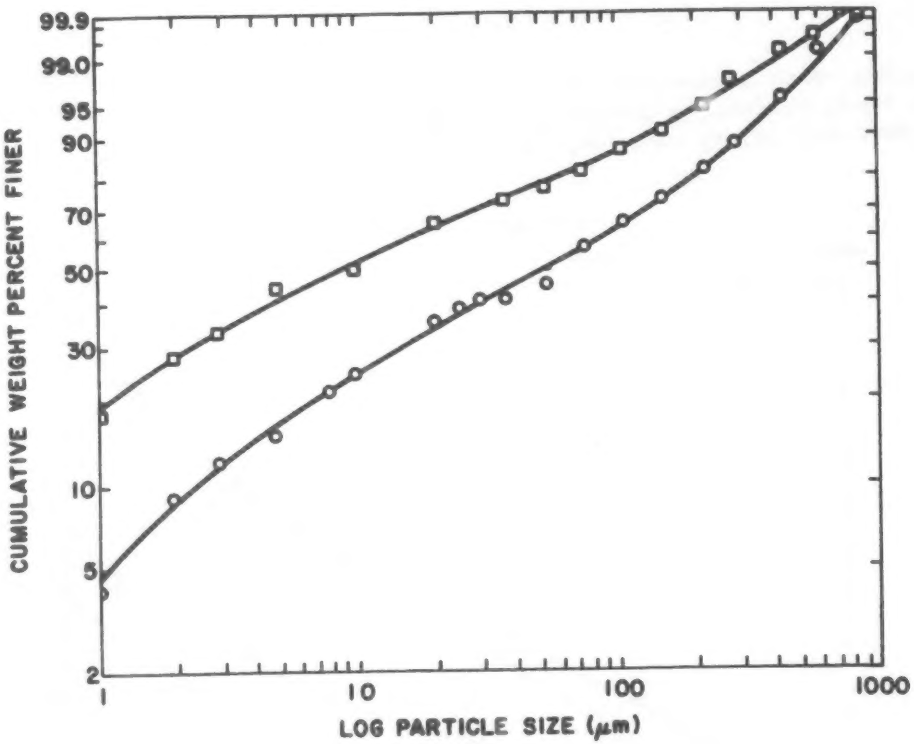

Figure 7. Particle size distribution of blackwater solids, sample no. L.F. C Pa 4. (Lower Freeport Seam, Cambria County, Pennsylvania, 80.4 Wt % coal)

○ Carbonaceous
□ Mineral matter

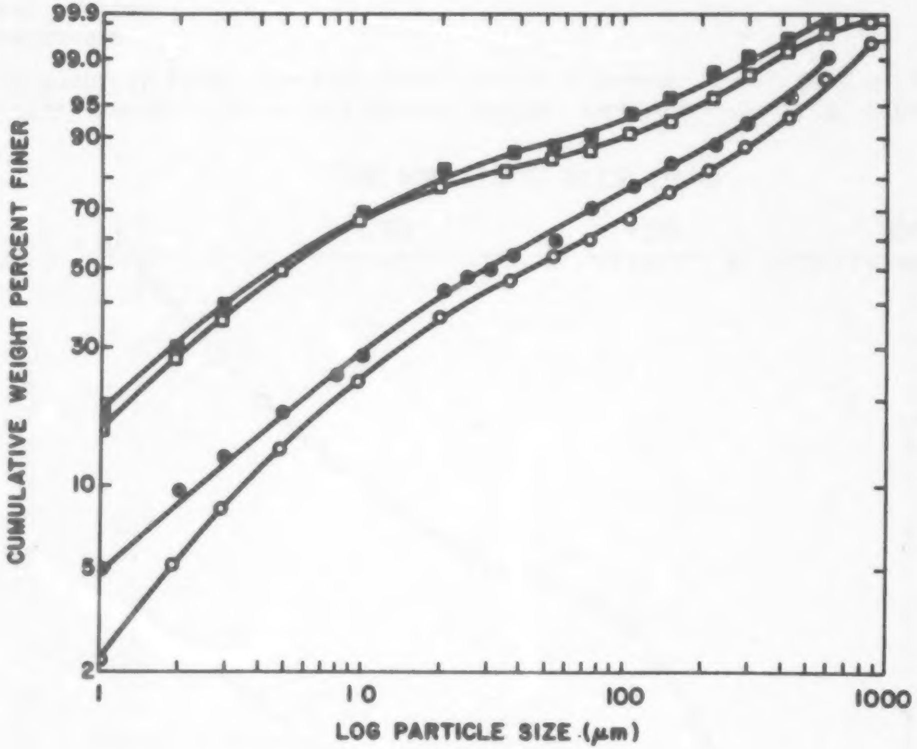

Figure 8. Particle size distribution of blackwater solids from the Pocahontas samples, sample no. Po. M WVa 5 and Po. W WVa 6. (Po. M WVa 5--#3, #4, #5, Pocahontas Seam, McDowell County, West Virginia, 70.9 Wt % coal; Po. W WVa 6--#3 Pocahontas Seam, Wyoming County, West Virginia, 63.9 Wt % coal)

Sample No. Po. M WVa 5

○ Carbonaceous
□ Mineral matter

Sample No. Po. W WVa 6

● Carbonaceous
■ Mineral matter

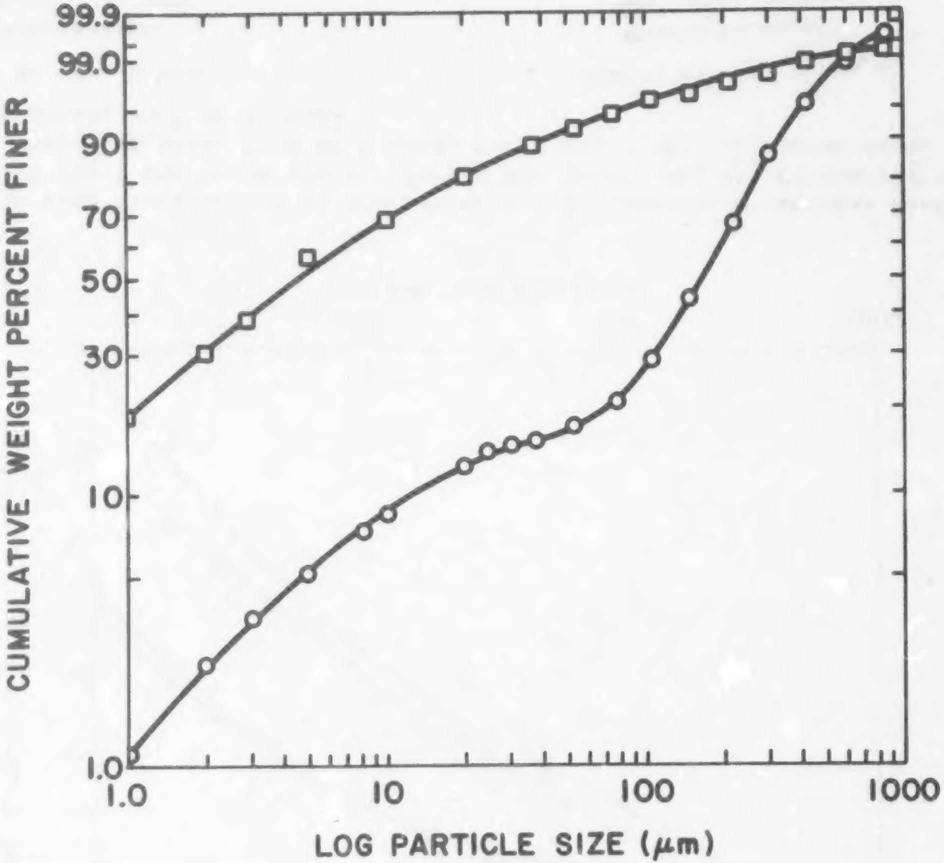

Figure 9. Particle size distribution of blackwater solids, sample no. Pi./L.F. H Oh 7. (75% Pittsburgh Seam/25% Lower Freeport Seam, Harrison County, Ohio, 84.1 Wt % coal)

○ Carbonaceous
☐ Mineral matter

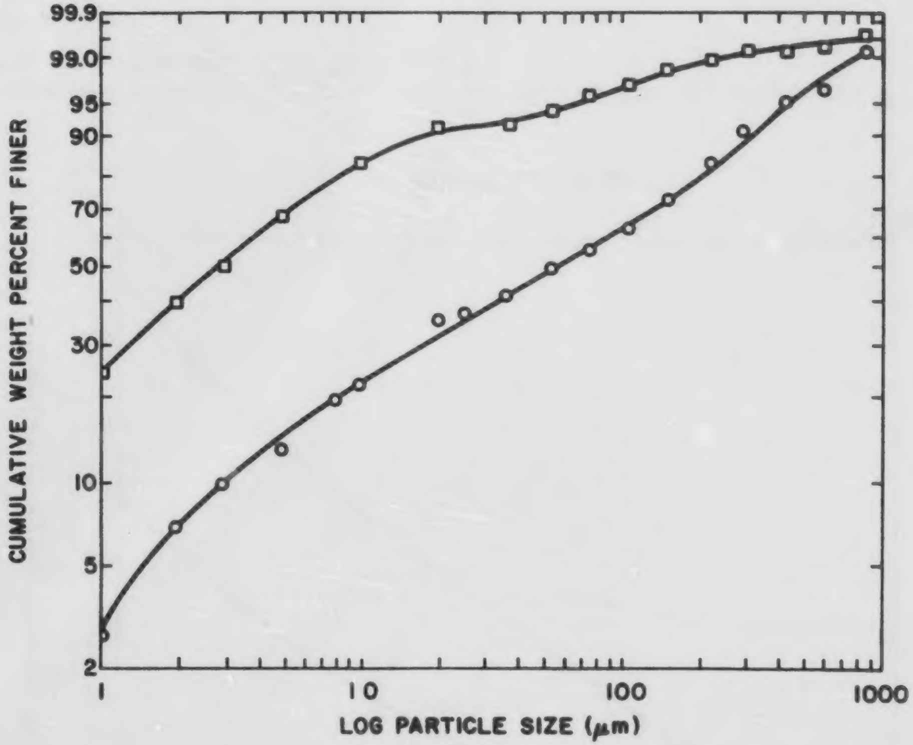

Figure 10. Particle size distribution of blackwater solids, sample no. E L Ky 8. (#2 Elkhorn Seam, Letcher County, Kentucky, 47.9 Wt % coal)

○ Carbonaceous
☐ Mineral matter

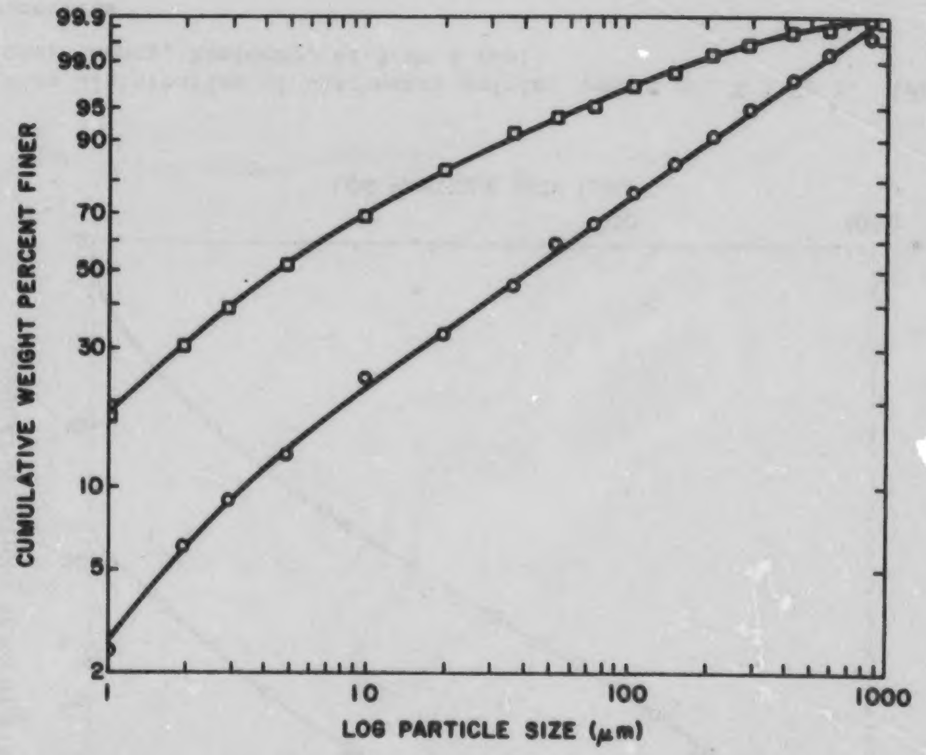

Figure 11. Particle size distribution of blackwater solids, sample no. Pr. J Ala 9. (Pratt Seam, Jefferson County, Alabama, 72.3 Wt % coal)

○ Carbonaceous
☐ Mineral matter

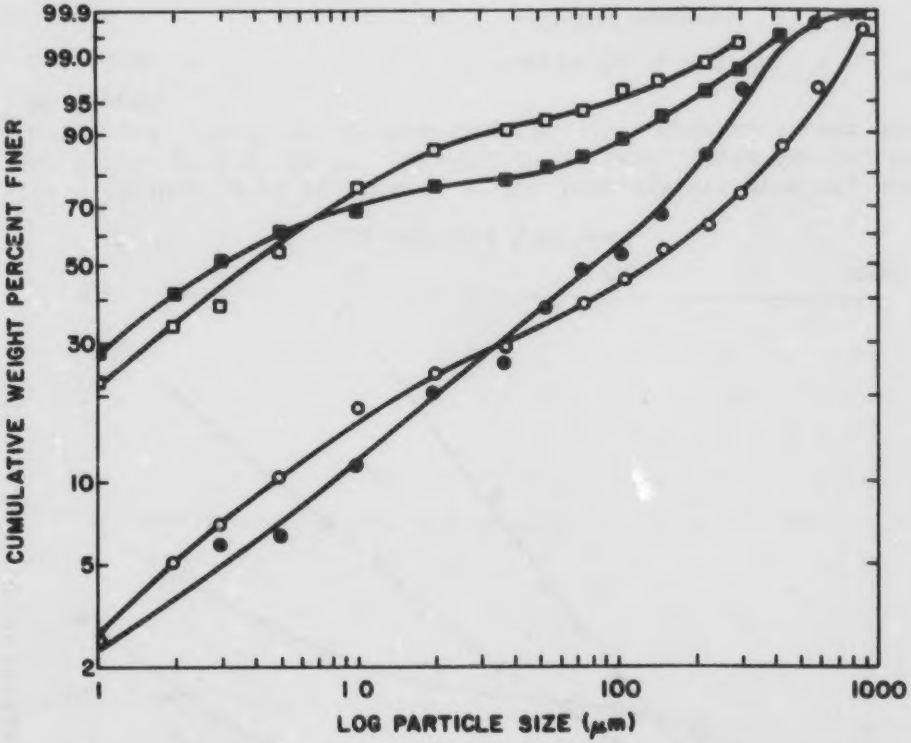

Figure 12. Particle size distribution of blackwater solids from Indiana and Illinois samples, sample no. I6/5 J Ill 10 and I6 W Ind 11. (I6/5 J Ill 10--#5, #6, Illinois Seam, Jackson County, Illinois [30], 19.0 Wt % coal; I6 W Ind 11--#6 Indiana Seam, Warrick County, Indiana [30], 28.9 Wt % coal)

Sample No. I6/5 J Ill 10

○ Carbonaceous
☐ Mineral matter

Sample No. I6 W Ind 11

● Carbonaceous
■ Mineral matter

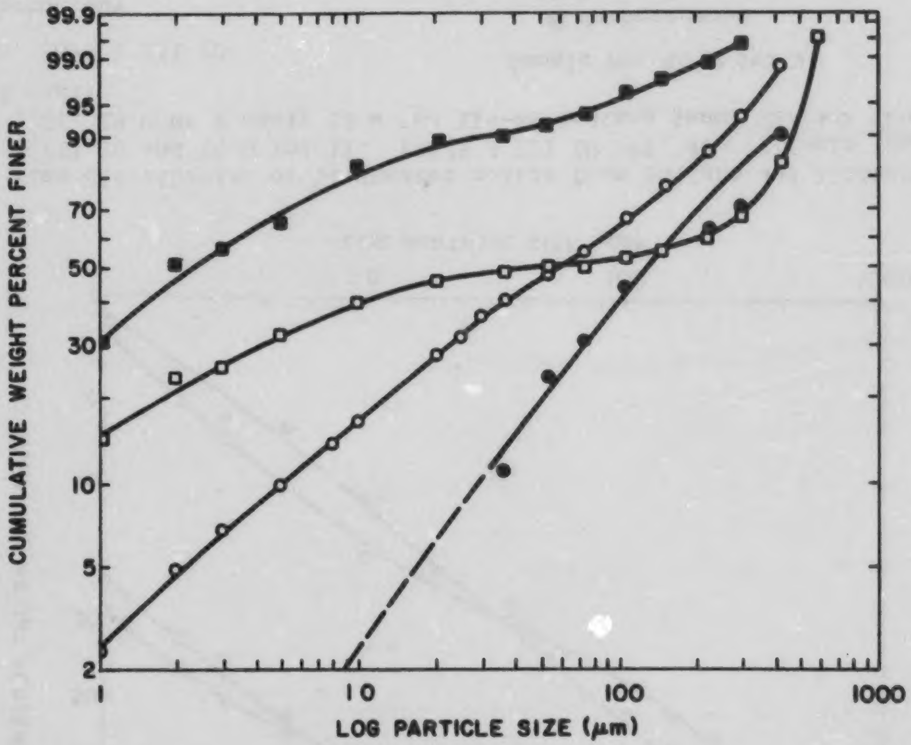

Figure 13. Particle size distribution of blackwater solids from western samples, sample no. B.D. L Wa and S/L.S. Ut 13. (B.D. L Wa--Big Dirty Seam, Lewis County, Washington [30], 27.2 Wt % coal; S/L.S. Ut 13--Somerset 'B', 'C', Colorado/Lower Sunnyside, Utah, 50.1 Wt % coal)

Sample No. B.D. L Wa 12

- ● Carbonaceous
- ■ Mineral matter

Sample No. S/L.S. Ut 13

- ○ Carbonaceous
- □ Mineral matter

400 mesh (37 μm) material. In this way, a region of overlap (37 to 74 μm) between the sieving and sedimentation results was obtained. As shown in Figure 5, the distributions obtained from both methods are in very good agreement.

The size distributions of the carbonaceous material from the different samples are also quite similar to each other. The carbonaceous material is somewhat more uniform than the mineral matter and the distributions therefore tend to have a smoother shape than those of the mineral material.

The shape of any size distribution is dependent upon the history of the sample, and this may explain the atypical nature of some of the samples, especially samples B.D. L Wa 12 and S/LS Ut 13. Sample B.D. L Wa 12 was from a settling pond and S/LS Ut 13 was minus 28 mesh refuse obtained from the refuse product. The other eleven samples were typically from thickener underflows from different preparation plants. Sample B.D. L Wa 12 contains finer material than any of the other samples. Thirty-one percent of its material was found to be less than 1 μm, while the next finest material was 19% minus 1 μm. The extreme fineness of this sample may be due to the fact that the sample came from a slurry pond where the solids may have had a long period of time to settle. In addition, this sample contained a large amount of montmorillonite clay which tends to be extremely fine.

Sample S/LS Ut 13 contains a mineral fraction that was somewhat coarser than the other samples. Only 51% of its mineral material was less than 45 um while the next coarsest sample contained 70% less than 45 μm. The relative coarseness of this sample may have been a result of the method used to obtain the sample, i.e., by removing the minus 28 mesh fraction from the plant refuse by screening.

The size analysis for Samples I6/5 J Ill 10; I6 W Ind 11; and B.D. L Wa 12 were determined by Michael F. Placha (30). He used the same procedure that was previously outlined in Section III.C.

3. Comparison of Size Distributions

A notable feature of this particle size characterization work is the rather surprising similarity of the size distributions obtained from seemingly quite different samples. This similarity can be seen clearly in Figures 14 and 15 in which the mean size distribution of the first eleven blackwater samples was calculated for the mineral matter and the carbonaceous fractions, respectively. Samples 12 and 13 were not included because of their differences in their mineral composition and the method of sampling used. The first eleven samples are from preparation plants, in the East and Midwest, treating coal from seams belonging the the Pennsylvanian Period.

The dashed lines in Figures 14 and 15 correspond to one standard deviation about the mean, which indicates that the size distribution of the eleven samples falls into a relatively narrow band. This similarity was unexpected since the samples come from a

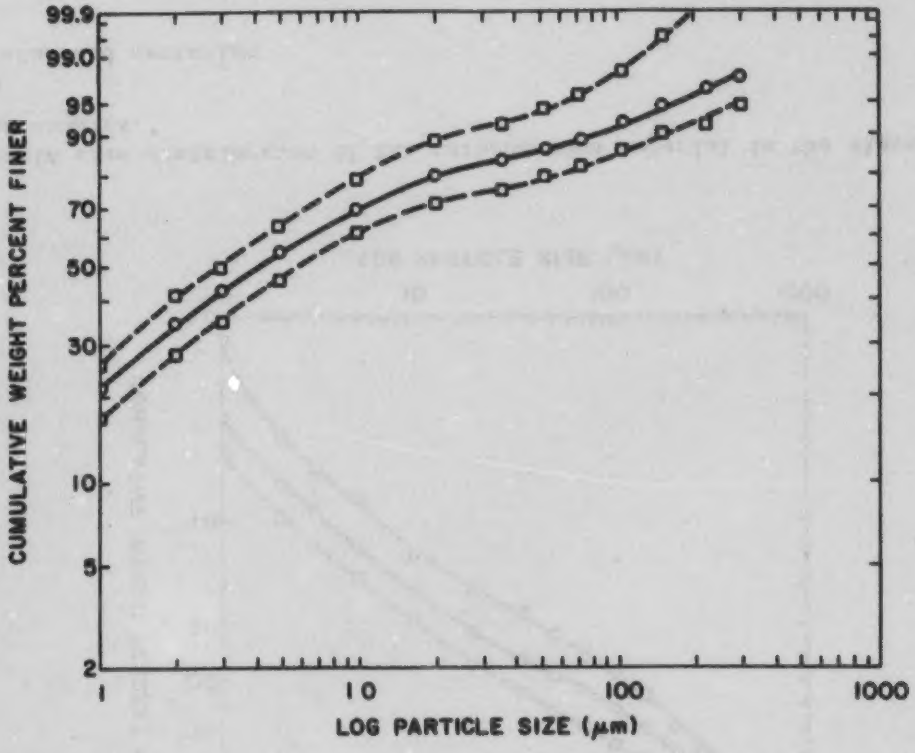

Figure 14. Mean particle size distribution of the mineral matter in the eleven eastern blackwater samples.

○ Mean
☐ One standard deviation

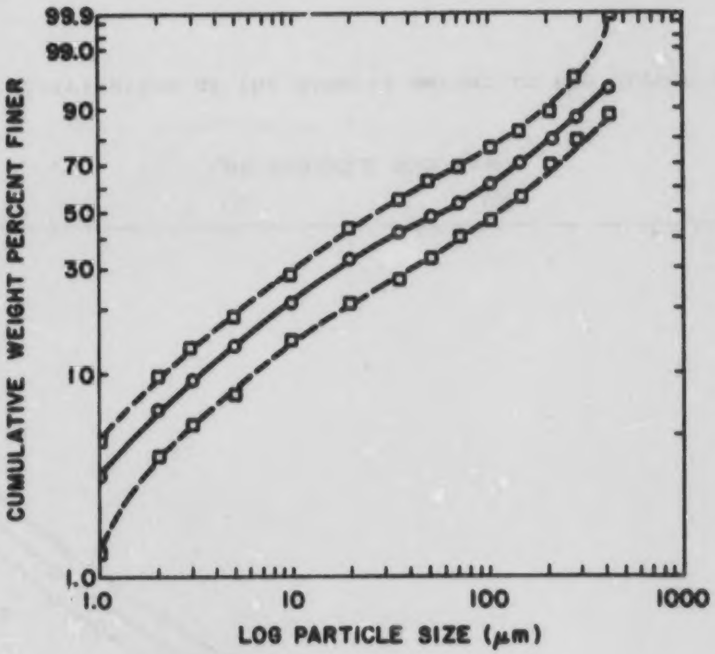

Figure 15. Mean particle size distribution of the carbonaceous material in the eleven eastern blackwater samples.

○ Mean
☐ One standard deviation

variety of coal seams, mining operations, and preparation methods. Although all eleven samples are from coal seams of the same geological period, their geographical area covers most of the Appalachian and some of the Mid-western states. Samples were obtained from both surface and underground mining operations with the majority of the samples coming from underground operations. A large variety of treatment methods were employed at the different preparation plants. Some of the plants have very simple circuitry in which only coarse coal was being cleaned while many of the plants were preparing metallurgical coal and therefore tend to have a more complex circuit in which fine coal is cleaned. The shape of the two mean size distributions are very different, with the mineral fraction consisting of a finer material than the carbonaceous material. The fineness of the mineral material was mainly due to the presence of a lot of clay, while the carbonaceous material contained essentially all coal and thus had a somewhat coarser size distribution.

4. Overall Size Distribution

For each sample an overall size distribution can be calculated from the separate size distributions of the mineral and carbonaceous material (given in Appendix D) and from their weight percent (given in Table 9). The combined size distribution for a sample can be calculated using the following procedure:

Example: Sample Pi W Pa 1

Data

Material	-400 Mesh	Wt% of Solids
Mineral	92.6	44.5
Carbonaceous	64.6	55.5

Percent of -400 mesh = (0.926 x 44.5) + (0.646 x 55.5) material in sample = 77.1 percent

This method was used to generate the data given in Table 13, except that the minus 44 μm (325 mesh) values were determined by interpolation from the size distribution plots since this value was not measured experimentally. Table 13 contains values for the amount of material that is less than 44 μm and 1 μm for each fraction and the total amount in each sample.

The overall size distribution for most of the thirteen blackwater samples is similar, especially for the eleven Eastern samples. There are a few samples that are finer or coarser than the others, but the majority of the samples show an unexpected similarity. The range of the minus 44 μm material in the thirteen blackwater samples is 28-86 percent, a 58 percent difference. If the two extreme samples are not considered, a range of 40-77 percent, a 37 percent difference, exists. Six of the thirteen samples have a range of 64-70 percent, only a 6 percent difference. It is interesting to note that the

Table 13. Particle size analysis of blackwater. (Weight percent less than 44 µm[a] and 1 µm)

Sample	Coal Fraction		Mineral Fraction		Total Sample	
	4 µm	1 µm	4 µm	1 µm	4 µm	1 µm
Pi W Pa 1	66	6.1	93	33	77	17
L.K.C. Pa 2	43	2.5	84	27	58	11
L.K.C. Pa 3	35	2.5	70	15	40	4
L.F.C. Pa 4	44	4.2	76	18	50	7
PoM WVa 5	62	5.0	89	18	70	9
PoW WVa 6	52	2.3	84	17	64	8
Pi/LFH Oh 7	16	1.1	90	19	28	4
EL Ky 8	47	3.0	93	25	69	14
PrJ Ala 9	54	2.8	93	43	65	14
I6/5J Ill.10	30	0.8	80	28	64	19
I6W Ind.11	32	5.2	91	12	66	9
BDL Wa 12	16	---	91	31	86	31
S/LS Ut 13	40	2.3	51	14	45	9
Mean	41	3.1	83	23	60	12
Range	16-66	0.8-6.1	51-93	12-43	28-86	4-31

---

[a] 44 µm equals 325 mesh.

two samples that have extreme values for the minus 44 μm, total material, are the two samples from the West. The reason for their difference is most likely due to the source of the samples and to the method of sampling.

A sub-sieve size distribution of the carbonaceous material in sample B.D. L Wa 12 was not determined since this material comprised less than 3.0 percent of the total material. A size analysis was made on the total sample, assuming the presence of such a small amount of carbonaceous material would not have any significant effect on the outcome of the analysis. This sample contained carbonaceous material that appeared to be highly oxidized, resulting in poor separation during froth flotation.

In most of the samples, the high clay content dominated the size characterization of the mineral material and influenced the overall size characteristics of the waste material. The thirteen samples produce a total mean size distribution of 60 and 12 weight percent minus 44 μm and 1 μm, respectively. The high percentage of fine material in the waste water may be an indication of the difficulty expected when treating the waste water. The mineralogical and size characteristics for each specific sample has been tabulated and given in Appendix E.

C. Surface Properties of Mineral Matter and Coal Contained in Blackwater

1. Introduction

The surface properties of the ash-forming minerals and the coal fractions from the blackwater samples were investigated using a Zeta Meter. The magnitude and sign of the surface charge of the blackwater constituents were determined as a function of pH in order to estimate the point of zero charge (PZC) for the different constituents. The zeta potential of the particles composing a suspension has an effect on the stability of that suspension, and an approximation of this effect is shown in Table 14. This approximation ignores the effects of particle size and ionic strength of the suspension, and assumes that all the particles are of the same surface polarity.

According to Table 14, a zeta potential of 5 to 10 mv offers fair agglomeration for material of similar surface polarity, with excellent agglomeration occuring at about 5 mv or less. Of course, it is the goal in the treatment of blackwater to destabilize the suspension, i.e., to agglomerate or flocculate the particles. One way to achieve this is to reduce the potential to near zero. Thus, a knowledge of the potential of the bulk suspension and the individual particles contained in the suspension is of great importance. For this study the mineral matter and carbonaceous fractions were initially studied separately. The fractionation procedure has previously been outlined in Section III.B.3a.

Table 14. Relationship between colloid stability and zeta potential. (after Riddick [43])

Stability	Zeta Potential[a], mv
Excellent agglomeration	5 mv
Fair agglomeration	5 to 10 mv
Threshold for agglomeration	10 to 20 mv
Moderate stability	30 to 40 mv
Good stability	40 to 60 mv
Excellent stability	60 mv and higher

[a] Helmholtz-Smoluchowski formula (43).

2. Mineral Fraction

Once the mineral constituents in the blackwater samples were identified, quantified, and their size distribution determined, the surface properties of the principal minerals were then characterized. The surface properties of some of the principal constituent minerals found in the blackwater, such as kaolinite, have been investigated in the past and are well known, and therefore were not investigated in detail here. However, the surface properties of especially the illites and chlorites are not available from the literature, and so these minerals were emphasized in this study.

a. Illite. The surface properties of illite clays from both illitic shales and from various blackwater samples were determined and compared. The illitic shales that were investigated were two samples from Fithian, Illinois: A. API Standard Clay #35; and B. 25-lb bulk sample; and C. One sample from Morris, Illinois, API Standard Clay #36.

The surface properties of the three illitic shales were investigated to establish the general behavior of illites. The pH-potential curves for the 'as-is' illite samples A and B, from Fithian, Illinois, were determined using distilled water (with HCl and NaOH as pH regulating agents) and the results of this study are shown in Figures 16 and 17. Note the similarity of these two curves which show a zeta potential of about -5 to -10 mv over the pH range of 3 to 8. Illite sample C from Morris, Illinois shows a

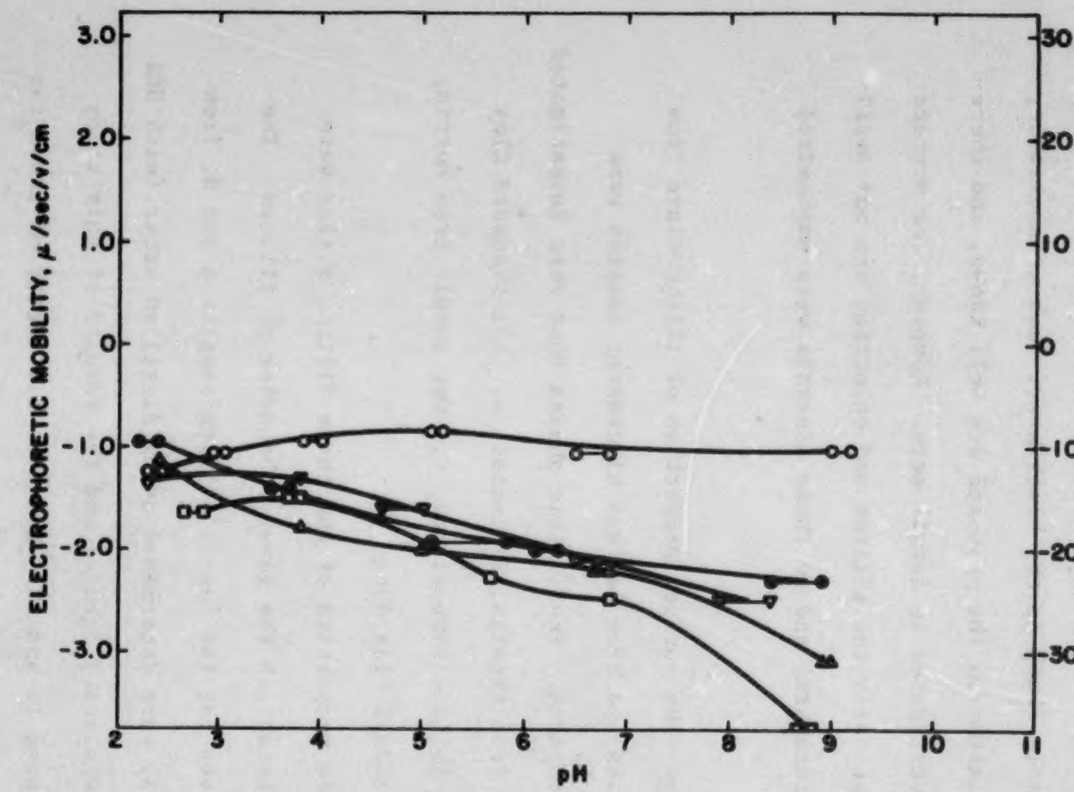

Figure 16. Electrophoretic mobility of illite sample (A) from Fithian, Illinois. The surface properties of the sample were investigated under the following conditions:

- ○ As is distilled water
- ● As is 1 x 10^{-2}M NaCl
- □ Acid washed
- △ Acid washed 1 x 10^{-3}M NaCl
- ▽ Acid washed 1 x 10^{-2}M NaCl

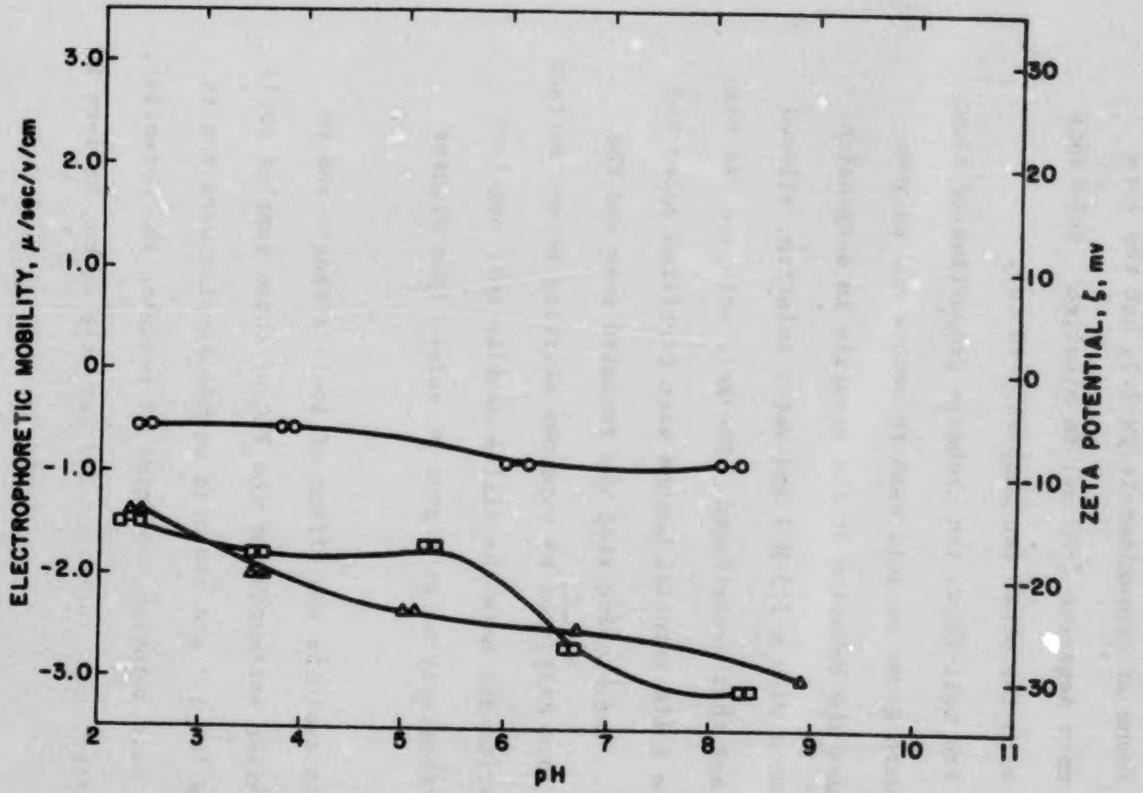

Figure 17. Electrophoretic mobility of illite sample (B) from Fithian, Illinois. The surface properties of the sample were investigated under the following conditions:

○ As is distilled water
□ Acid washed
△ Acid washed 1 x 10^{-3}M NaCl

somewhat different pattern (Figure 18). The change in surface potential with pH for this sample is much more pronounced than was found for the other two illite samples, not only was an isoelectric point found at approximately pH 2.2, but the zeta potential becomes more negative (-20 mv) in alkaline solutions than was observed with the other two samples (-10 mv).

Because of the well-known ion exchange properties of clays (14) the samples were given an acid wash to remove any cations that might influence the behavior of the minerals in suspension. The clays were washed with a 1:5 HCl and water solution, stirred for 5-10 minutes and then centrifuged. The acid solution was then poured off and the solid material washed with distilled water and centrifuged again. The washing step was repeated once and the illitic material then dispersed by vigorous stirring before surface analysis. This acid wash made the illite samples more negative in each case, increasingly so at higher pH values (see Figures 16-18).

In order to evaluate the effect of ionic strength and to determine if a better estimation of the PZC of these samples could be made, both the 'as is' and the acid washed samples were run in 10^{-3} or 10^{-2} M/L salt solution. Outside of reducing the potential, as would be expected, this technique did not help as may be seen in Figures 16-18.

A sample of illitic material from different blackwater mineral matter fractions was obtained from the material used in the

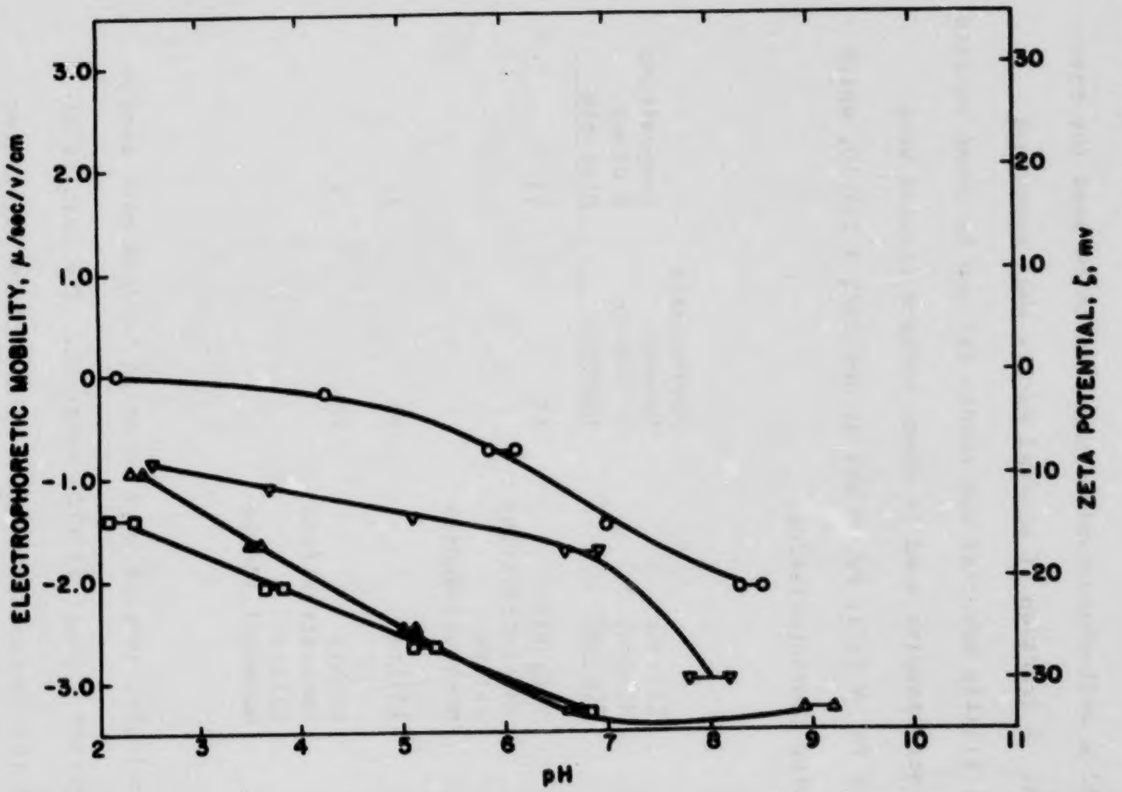

Figure 18. Electrophoretic mobility of illite sample (C) from Morris, Illinois. The surface properties of the sample were investigated under the following conditions:

○ As is distilled water
□ Acid washed
△ Acid washed 1 x 10^{-3}M NaCl
▽ Acid washed 1 x 10^{-2}M NaCl

identification and quantification process. X-ray analysis provided both a careful identification and a quantification of this illitic material, and the use of the centrifuge layering technique allows the selection of a well-characterized material to be used for these surface studies. A fraction of mineral matter that contained essentially all illitic material was chosen for use in these surface studies. The three samples used in these surface studies were samples numbered Pi. W Pa 1; Po. M WVa 5; and I6/5 J Ill 10, which have the following characteristics:

Sample	Illitic Mineral Present	Approximate Mineral % Illitic Minerals	Composition % Other Minerals
Pi. W Pa 1	Slightly interstratified illite-montmorillonite	65	33
Po. M WVa 5	Illite	80	21
I6/5 J Ill 10	Highly interstratified illite-montmorillonite	90	7

These particular samples were selected because each sample contained a different type of illitic material. The results of these studies of the surface properties of the three blackwater illites are shown in Figure 19. The surface charge of the three materials remains negative until pH 2.5 where the PZC for Po. M WVa 5

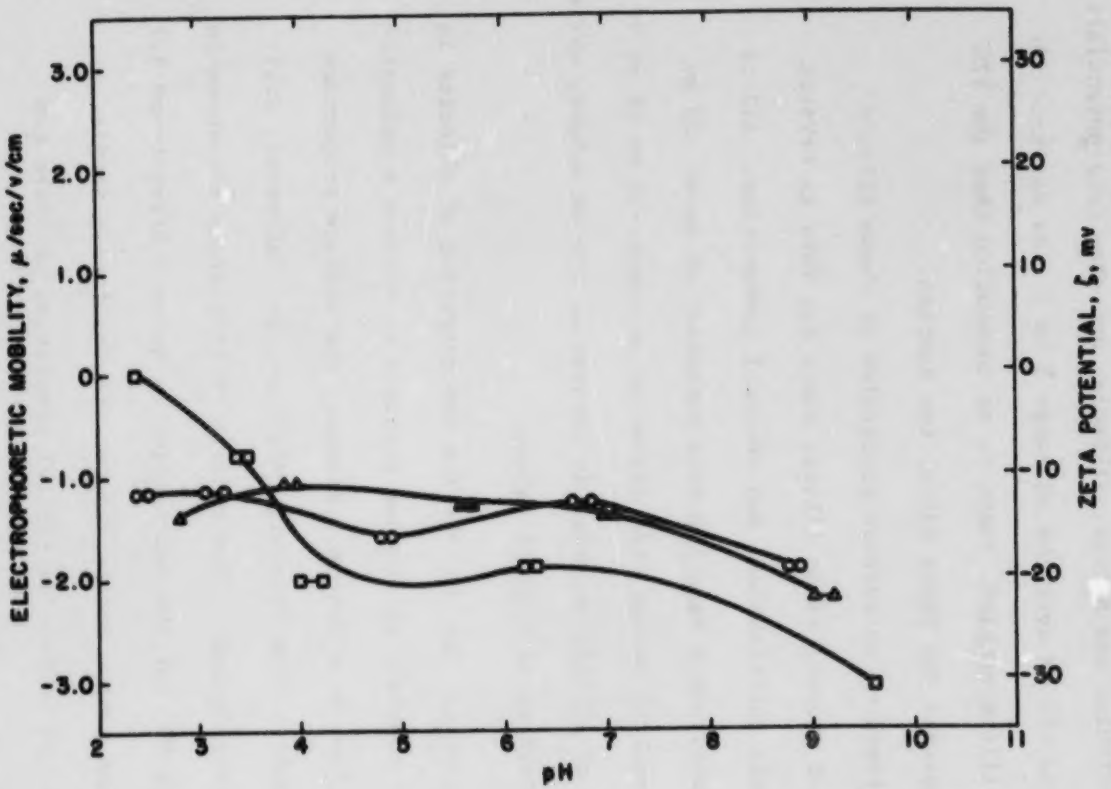

Figure 19. Electrophoretic mobility of illitic material from the following blackwater samples.

○ Pi. W Pa 1
□ Po. M WVa 5
△ I6/5 J Ill 10

occurred. The curves for samples Pi. W Pa 1 and I6/5 J Ill 10 are seen to generally follow the pattern of the standard illite samples from Fithian and Morris, Illinois, and show zeta-potentials of about -15 to -10 mv over the pH range 3 to 7. As was true for the standard illite samples, there is no indication that the PZC is being approached for these latter two samples.

The difference in surface properties of these illitic minerals is not unusual since illitic clays can vary in crystal structure, ionic substitution, and chemical composition. All of the illites developed a negative zeta potential of about -10 mv or higher at neutral pH and this increases to about -20 mv at pH 9. Agglomeration of illitic material is favored at low pH values, while stability is favored at high pH values.

b. Chlorite. Due to the low concentration of chlorite in the blackwater samples, it was not possible to produce a chlorite-rich fraction from this source. However, the surface properties of chlorite samples from Ishpemig, Michigan, and Calaveras, California were investigated. The results of this study are shown in Figure 20. The PZC for the two samples is quite different--pH 5.7 for the Michigan sample and pH 2.5 for the California sample. Differences in the surface electrical properties of these two samples is not unexpected in view of the wide variation in composition and cyrstallinity of chlorite (14).

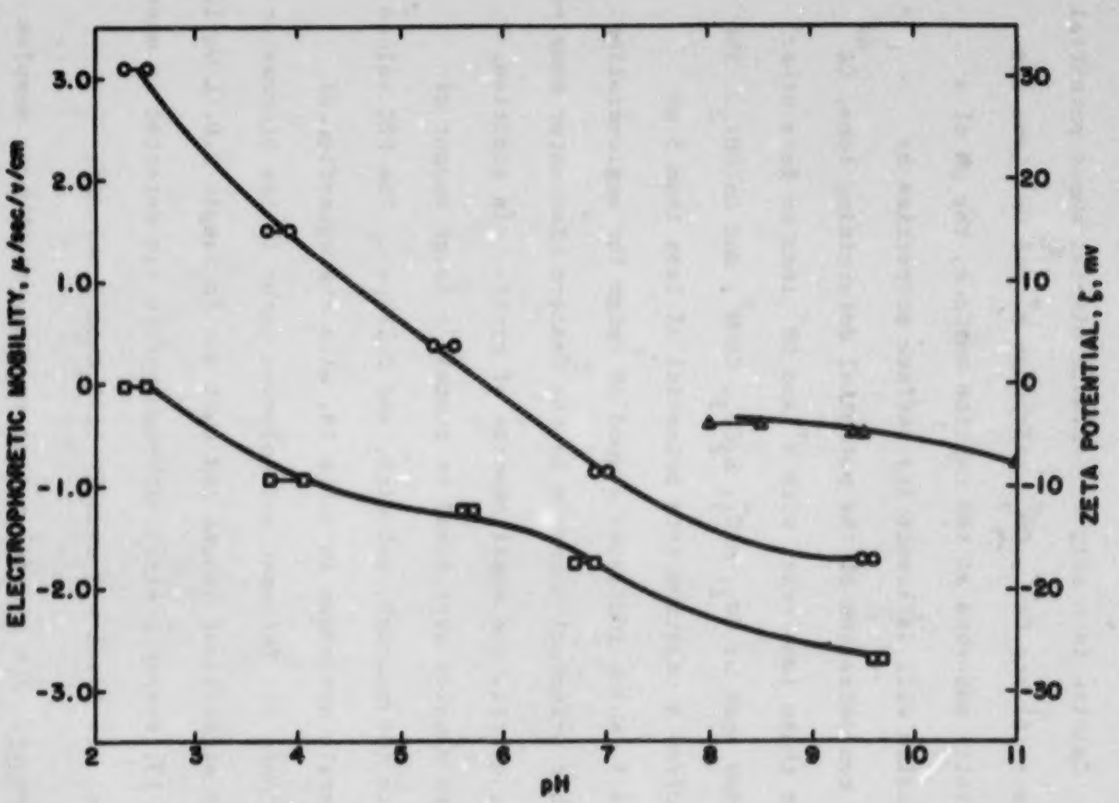

Figure 20. Electrophoretic mobility of the following minerals, chlorite and limestone.

○ Chlorite, Ishpeming, Michigan
□ Chlorite, Calaveras, California
△ Valentine Limestone, Centre County, Pennsylvania

c. Other minerals. The surface properties of limestone in alkaline solution were also investigated and the data are shown in Figure 20. Calcite is a slightly soluble mineral whose potential determining ions (4) are Ca^{++}, $CO_3^{=}$. Although H^+ and OH^- ions are not preferentially adsorbed at the calcite surface, the pH of a calcite suspension will influence its surface properties by effecting the concentration of the potential determining ions, Ca^{++} and $CO_3^{=}$, since these ions react with H^+ and OH^- ions to form other chemical species such as CO_2, HCO_3^-, H_2CO_3, $CaOH^+$, and $Ca(OH)_2$. The limestone acquired a negative zeta potential of less than 5 mv from pH 8 to 9.5, which indicates a good pH range for agglomeration.

The other principal minerals in the Eastern blackwater samples are kaolinite, quartz, and small amounts of pyrite. In addition, the two Western samples were found to contain a large amount of montmorillonite (bentonite), dolomite, and feldspar. The PZC values for these minerals are shown in Table 15, with the exception of pyrite. Only once did feldspar and dolomite occur in the blackwater samples in any significant amount and that was in Sample B.D. L Wa 12 and S/L.S. Ut 13, respectively. Although pyrite was detected in most of the samples, its level was usually less than 5 percent.

d. Summary. The mineral matter in these blackwater samples consists of two types of minerals; silicates and non-silicates. The silicate minerals, in turn, consist of two subgroups:

Table 15. Point of zero charge for some minerals found in blackwater. (Literature values) (Potential determining ions are H^+ and OH^-)

Mineral	PZC
Kaolinite (18)	pH 3.4
Quartz (11,28)	pH 2 to 3.7
Montmorillonite (18) Bentonite	<pH 3
Calcite (35)	pH 8 to 8.5
Dolomite (26)	>pH 8 + 10 mv or higher
Feldspar	
Albite (9)	pH 2.0
Oligoclase (26)	pH 1.0
Microcline (9)	pH 2.4
Orthoclase (26)	pH 1.0

1. Layer Structure Silicates--
   illitic, kaolinite, montmorillonite clays and chlorite.

2. Framework Silicates--
   quartz and feldspar.

Calcite is the most dominant mineral in the non-silicate group with lesser amounts of dolomite and pyrite. The surface properties of all the silicate minerals present are somewhat similar in that the potential determining ions for these minerals are H^+ and OH^-, and their indicated point of zero charge occurs below pH 4. The minerals in the non-silicate group are indirectly affected by the concentration of H^+ and OH^- ions because of the effect of pH on their potential determining ions through the CO_2-HCO_3^--$CO_3^=$ and H_2S-SH^--$S^=$ equilibria and through precipitation of metal ions by hydroxyl ions.

Since the bulk of the mineral matter in the blackwater samples is the clay mineral group, the surface properties of these clay minerals will greatly affect the surface properties of the suspension as a whole. This effect is further magnified because of the small particle size and high surface area of the clays. Manipulation of the pH of blackwater suspensions will thus have a strong influence on the zeta potential of the contained mineral matter, and therefore offers a means of controlling the agglomeration of this mineral matter. Alkaline suspensions tend to develop large negative zeta potentials for most silicate minerals which, in turn, would tend to decrease the agglomeration for these minerals. This would leave slow settling fine particles suspended in the water and result in a high turbidity of the water to be recycled. The agglomeration of most of the mineral matter found in blackwater, the silicates, should be enhanced as the pH of the suspension is lowered.

3. Carbonaceous Material

The large carbonaceous content of most of the blackwater samples suggests that the surface properties of this material will exert an important influence on any blackwater treatment processes. The surface properties of a material as heterogeneous as coal vary depending on rank (41), lithotypes (8), and mineral matter content of the coal (3).

Campbell and Sun studied the effect of pH on the electrical properties of coal surfaces and concluded that hydronium and hydroxyl ions behave as potential determining ions (8). The effects of these ions on different lithotypes produced a variety of results, as is shown in Figure 21. The PZC for the whole coal sample, Pittsburgh seam, Ellsworth, Pennsylvania, is pH 4.6. The zeta potential of the whole coal sample is negative for pH values above 4.6 with the magnitude of the potential increasing significantly as the pH becomes alkaline. Not only do the surface properties of coal depend on its rank and lithotype, but also on the degree of oxidation of its surface (41). The effects of oxidation on surface properties

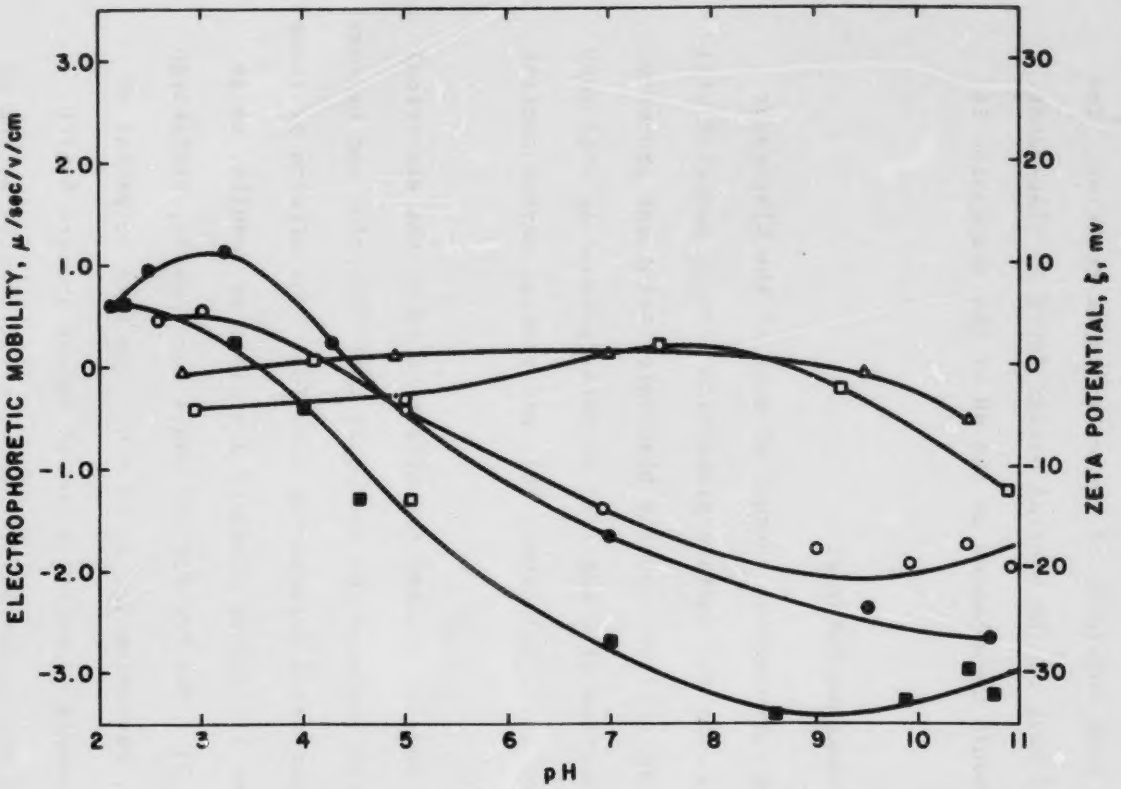

Figure 21. Variation of zeta potential with pH for Pittsburgh seam coal and its lithotypes. (after Campbell and Sun) (8)

1 Fusain
2 Gangue
3 Durain
4 Whole coal
5 Vitrain

of a high volatile A bituminous vitrain can be seen in Figure 22. These results indicate that increases in the degree of oxidation of coals increase the negative value of the zeta potential and lower the PZC.

The surface properties of carbonaceous material taken from several of the blackwater samples studied in this report were investigated. A direct measurement of the surface properties of the carbonaceous material was not performed since the samples were obtained from a flocculated thickener underflow. The effect of any flocculants that may have contaminated the coal surface was minimized by taking only the plus 400 mesh carbonaceous fraction and grinding it to near colloidal size to achieve a relatively clean surface. The surface properties of this material from six different blackwater samples were then investigated as a function of pH. The results are shown in Figures 23 and 24.

The results for all of these samples are roughly similar with an indicated PZC at pH 2.5 to 4.0 for all of the samples except for that from the Lower Kittanning seam (L.K. C Pa 2). They thus follow the general pattern established by Sun and co-workers (8,41) for fresh and oxidized coal. In actual practice one might expect the particles contained in blackwater to have surface properties more closely approximating those of oxidized coal (Figure 22).

In order to characterize, more thoroughly, the nature of the carbonaceous material contained in blackwater, the pH-zeta

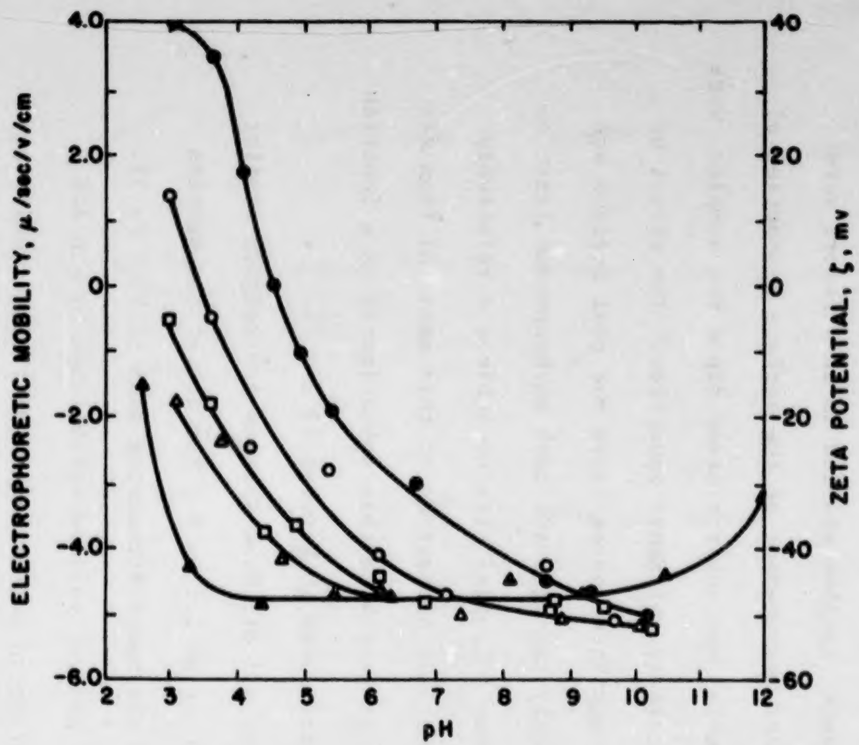

Figure 22. Effect of oxidation time on electrokinetic behavior of HVA-bituminous vitrain. (after Wen and Sun) (41)

HVA bituminous vitrain oxidation time at 125°C, Hr

● 0
○ 24
□ 48
△ 120
▲ 380

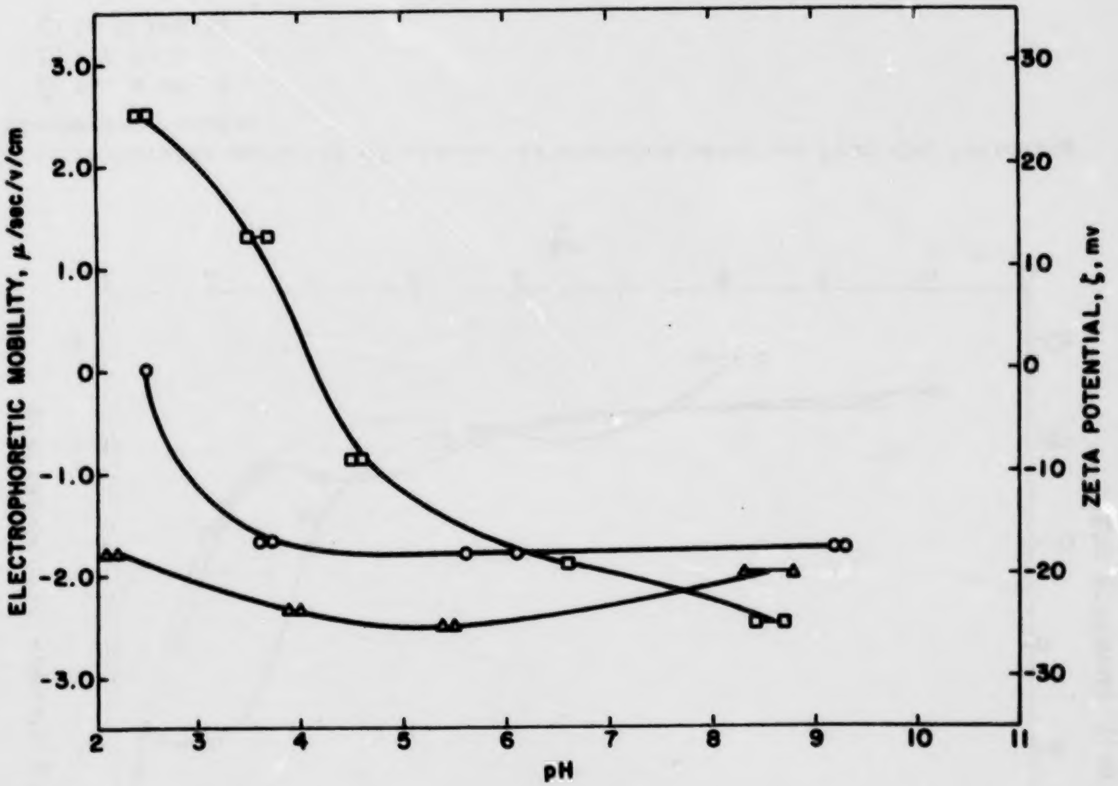

Figure 23. Electrophoretic mobility of coarse carbonaceous material from the following blackwater samples.

○ Pi. W Pa 1
△ L.K. C Pa 2
□ Pi./L.F. H Oh 7

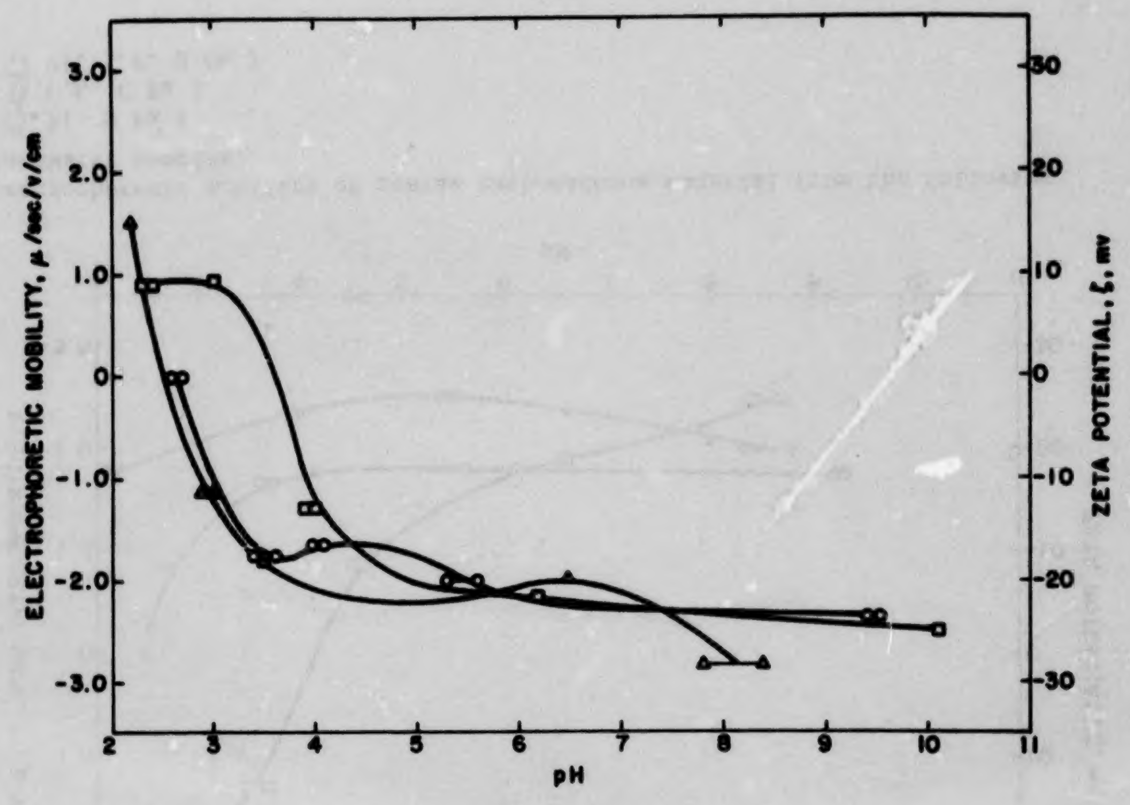

Figure 24. Electrophoretic mobility of coarse carbonaceous material from the following blackwater samples.

△ Po. W WVa 6
□ E L Ky 8
○ I6 W Ind 11

potential curves were determined for coal selected from three of the seams from whence came the blackwater. These seams are the Pittsburgh (Pi. W Pa 1), Lower Kittanning (L.K. C Pa 2), and Lower Freeport (L.F. C Pa 4). The results shown in Figure 25 indicate a pattern for fresh coal substantially different than that shown in the other figures. It definitely indicates that the coal taken from the blackwater samples was oxidized. Oxidized coal in a froth flotation circuit will tend to report to the tails and thus end up in the primary effluent of a preparation plant. The flotability of coal decreases as it becomes oxidized by weathering (36).

The surface properties of the carbonaceous materials contained in blackwater depend on a number of factors such as the rank, lithotype, and degree of oxidation of the particular coal sample. The zeta potential of most coals is negative in alkaline solution and the potential decreases as the pH is lowered. The PZC of a particular coal will depend on the composition of the coal and the degree of oxidation of the surface has acquired, with the PZC becoming lower as the degree of oxidation increases. Therefore, in the absence of specific flocculating agents such as alum, lime, starch, synthetic polymers, the agglomeration of most coal suspensions will be enhanced as the pH of the coal slurry becomes moderately acidic because of the lower zeta potential. The optimum pH range for agglomeration to occur for a particular coal will depend on the specific properties of that material, most especially its degree of surface oxidation. However, it appears that an

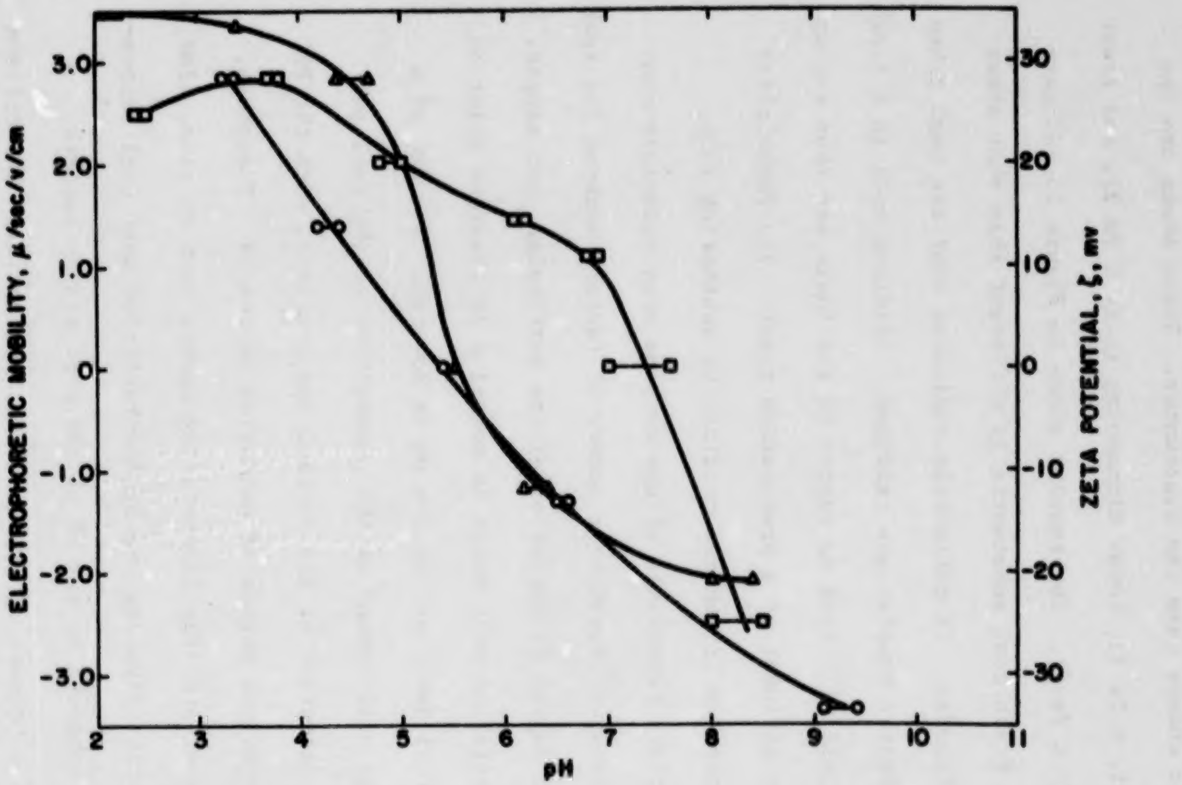

Figure 25. Electrophoretic mobility of hand-picked coal samples.

○ Pittsburgh seam
□ Lower Kittanning
△ Lower Freeport

alkaline pH for most coals results in a high negative zeta potential and thus a decrease in the ability to agglomerate. The best pH for flocculation of coal by pH control alone would be pH 5 to 7 for fresh coal and pH 2 to 4 for oxidized coal. The PZC value for fresh coal is substantially different from that of the mineral matter, whereas for the oxidized coal the optimum pH for flocculation, about pH 2, is similar to that of the mineral matter.

4. Surface Properties of Blackwater Slurries

Miller and Deurbrouck (24) analyzed the surface properties of blackwater slurries from four different coal seams--Upper Freeport, Hernshaw, Pocohontas No. 3, and Pittsburgh. The slurries were obtained from refuse thickener feed and did not contain any flocculants, but some of the samples did contain flotation reagents. The samples were dried to prevent disintegration of the solids during storage. The results of this study are shown in Figure 26.

The surface properties of the four slurries are roughly similar for pH values below 10. The PZC for the four samples occurs near pH2 and are similar to those of an oxidized coal in the region below pH 10. The ash content of the slurries ranged from 16.7 to 54.2 percent, indicating that the slurries contained much carbonaceous material. If oxidized, this carbonaceous material would produce a zeta potential curve similar to those obtained in the present study.

The surface properties of an unflocculated thickener feed, obtained from the same preparation plant as was blackwater sample

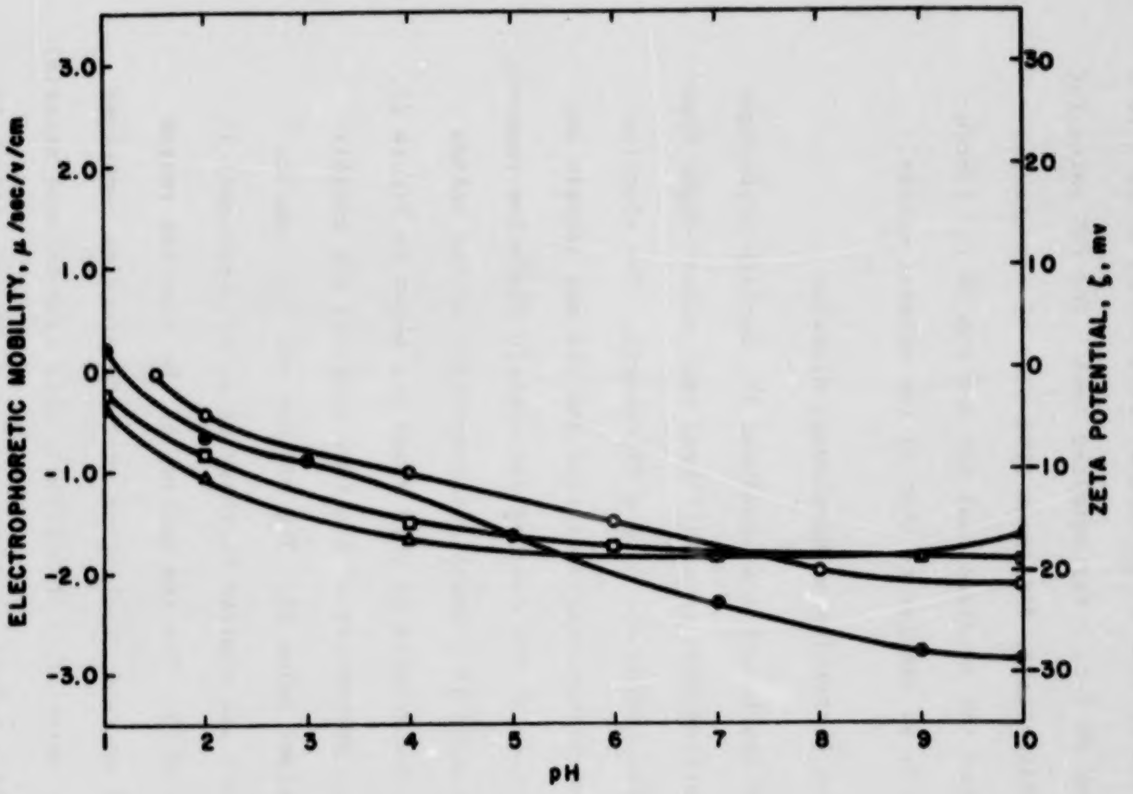

Figure 26. Zeta potential of blackwater slurries from different seams. (after Miller and Deurbrouck) (24)

△ Hernshaw seam
□ Pittsburgh seam
● Pocahontas #3 seam
○ Upper Freeport seam

L.K. C Pa 2, were studied, and the results of this analysis are shown in Figure 27. About 60 percent of the solid material in this sample was carbonaceous, and the balance was mineral matter. A total of 30 randomly picked particles were measured, and the data obtained were used to calculate the mean zeta potential at a particular pH range. Table 16 gives a tabulation of the variation in electrophoretic mobility for the various particles measured. Note that electrophoretic mobilities of most of the particles are similar, suggesting that the surface properties of most of the material are similar.

The zeta potential of the material was not significantly effected by varying the pH of the suspension. Since the zeta potential of this slurry did not vary significantly from -10 mv as the pH was varied from pH 2.2 to pH 9 (see Figure 27).

This insensitivity of the surface potential of this material may be real or may be due to adsorbed compound such as flotation reagents, e.g., frother. Flotation reagents would tend to contaminate the surface of the particles and modify the surface properties.

In this regard, one possible explanation for the differences between the present results and those of the Miller and Deurbrouck study may be the manner in which the slurries were stored. In the Miller-Deurbrouck study, the four slurries were stored in a dry form, while in the present study, the sample was stored in a slurry form. Drying the slurries may have caused the organic

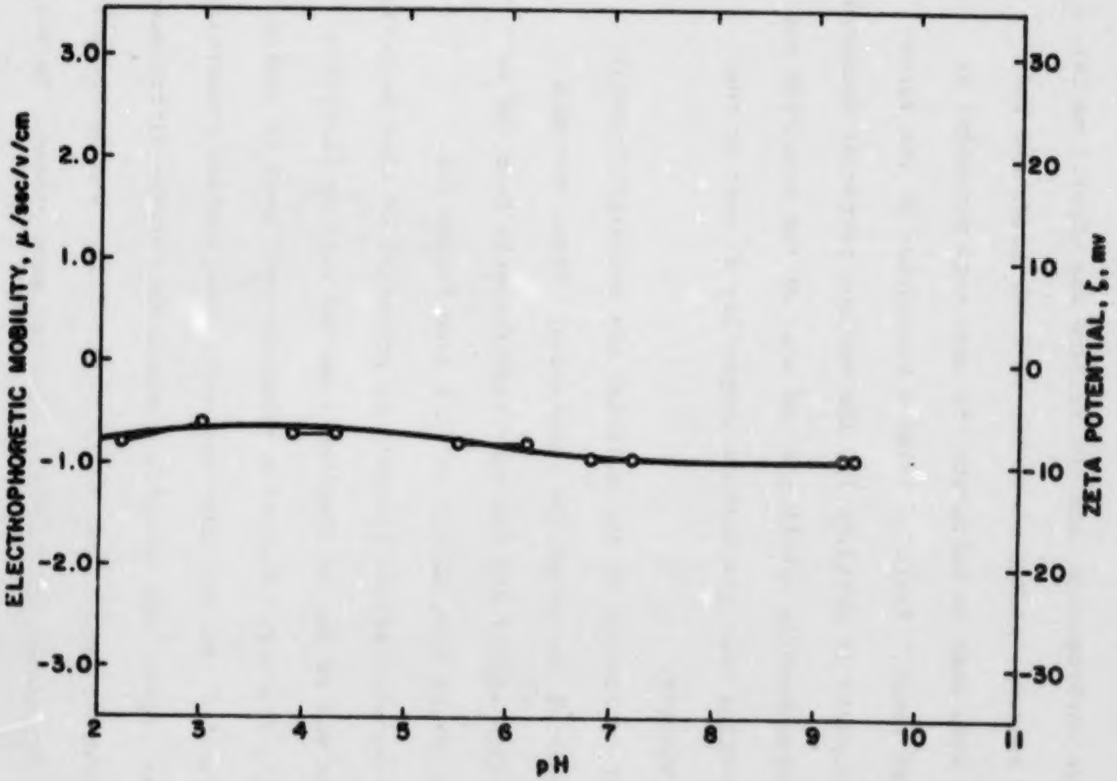

Figure 27. Electrophoretic mobility of an unflocculated thickener feed from a plant treating Lower Kittanning coal.

○ L.K. C Pa 2

Table 16. Electrophoretic mobility of a blackwater sample from a preparation plant treating Lower Kittanning coal. (Percentage of the 30 particles counted versus electrophoretic mobility)

Electrophoretic Mobility (Negative)	Percent of Particles				
	pH 3.0	pH 3.9-4.3	pH 5.5-6.2	pH 6.8-7.2	pH 9.3-9.4
0.50 - 0.58	16.7	10.0	---	10.0	---
0.58 - 0.66	30.0	33.3	23.3	3.3	3.3
0.66 - 0.80	23.3	26.7	36.7	26.7	20.0
0.80 - 1.00	10.0	13.3	20.0	13.3	36.7
1.00 - 1.33	6.7	10.0	13.3	20.0	26.7
1.33 - 2.00	0.0	0.0	6.7	16.7	13.3
Mean Electrophoretic Mobility (Negative)	0.64	0.70	0.80	0.95	0.97
Equivalent Zeta Potential mv (Negative)	2.5	9.3	10.6	12.6	13.0

flotation reagents to be destroyed or modified whereas this would be very unlikely to occur when the sample is stored in slurry form.

5. Summary

Generally blackwater consists of a large amount of carbonaceous material together with mineral matter that is predominantly silicates such as clays and quartz. The potential determining ions for most of this material are hydronium and hydroxyl ions. While the PZC for the different coals and silicate minerals are not the same, still most of the materials present in blackwater, except carbonates, have a PZC below pH 5. Generally, the zeta potential for most constituents found in blackwater is decreased as the pH is lowered, thus favoring agglomeration. This, of course, applies only to those systems where specific inorganic or organic flocculants are not added.

V. SUMMARY AND CONCLUSIONS

Characterization of the fine solid material in the primary effluent from coal preparation plants provides the basis for a better understanding of the problems associated with treating "blackwater." The present study was made to obtain a comprehensive characterization of the blackwater solids from coal preparation plants. The suspended solids from thirteen blackwater samples, representative of the major United States coal seams where wet preparation methods are used, were characterized by mineralogical content, particle size distribution, and surface properties.

The conclusions from this work are as follows:

A. Mineralogical Composition

1. Blackwater solids consist of two types of material--carbonaceous and mineral--of distinctly different chemical and physical properties.

2. Based on mineralogical similarities, the samples were divided into two groups: those from the Eastern half of the United States (Appalachian and Midwestern coal fields) and those from the Western half. The mineralogical content of the eleven Eastern samples was similar, while the two Western samples were

different from the Eastern ones, as well as from each other. The Eastern samples show marked similarities since they are all derived from coals of the Pennsylvanian period.

3. For all eleven Eastern blackwater samples tested, the carbonaceous content amounted to approximately 60% of the total weight of the blackwater solids. These studies showed that it is possible to remove, by froth flotation, essentially all of this carbonaceous (coal) fraction from the blackwater, and that the quality of this coal is such that it could be blended with the coarse clean coal without significantly altering the quality of the total product.

4. Additional clean coal may be recovered from current blackwater discharges from preparation plants by a more extensive use of the flotation process.

5. The average ash content of the carbonaceous fraction removed by froth flotation was 11 percent, as compared to an average of 41 percent asn in the as received blackwater samples.

6. The mineral fraction of the blackwater solids from Eastern and Midwestern coal fields contains largely illitic clays together with lesser amounts of kaolinite, quartz, calcite, chlorite, and pyrite. Minor amounts of dolomite, feldspar, rutile, or siderite were found in some of the samples.

7. The average mineralogical composition of the mineral matter fraction from blackwater solids of the eleven samples representative of the 'Eastern' coal fields can be summarized as follows:

Principal Minerals, Percent

	Illitic	Kaolinite	Chlorite	Calcite	Quartz	Pyrite
Average	55	11	4	12	15	4
Range of Average	47-65	6-22	0-7	0-22	8-22	1-10

Blackwater from plants treating coals dating from the Pennsylvanian period may be expected to have a mineral composition similar to this.

8. The high illitic clay content in the Eastern blackwater samples indicates that a large amount of the mineral material in the blackwater is of shale origin. Since shaley material is usually soft, and would decompose easily during processing, its presence in the blackwater effluent from a coal preparation plant is virtually assured.

9. The samples studied from West Virginia, Kentucky, and Alabama contained an "illitic" material of relatively good crystallinity with very little or no interstratification of montmorillonite

with the illite, whereas the samples tested from Pennsylvania, Ohio, Indiana, and Illinois contained an illitic material of varying crystallinity and interstratification.

10. The two Western samples have a different mineralogy than do the eleven Eastern samples studied. Both Western samples contain a large amount of montmorillonite clay. The unique mineral content of these two samples may be attributed to the fact that these coal seams belong to two different geological periods--the Washington sample (B.D. L Wa 12) from the Tertiary and the Colorado/Utah sample (S/L.S. Ut 13) from the Cretaceous.

11. Montmorillonite clay, such as that found in the Western samples, is often more difficult to flocculate efficiently than are illitic and kaolin clays, and a higher turbidity in the recycled water from plants treating these Western coals is to be expected.

12. The primary control on the composition of the mineral matter contained in blackwater is shown to be the composition of the adjacent strata which becomes incorporated into the run-of-mine coal during mining.

13. The differences in the carbonaceous content from sample to sample in the thirteen blackwater samples is more than likely due to differences in the mining and preparation methods employed at the different mines rather than to a difference in the type of coal being mined.

14. The average ash content of pure mineral matter of a typical Eastern sample is about 87 percent. The remaining 13 percent loss is due to the formation of H_2O, CO_2, SO_2, etc. upon heating.

B. Particle Size Analysis

1. Carbonaceous (coal) and mineral fractions from the different blackwater samples produce two distinct size distributions. The carbonaceous fraction is consistently coarser than the mineral matter fraction. On the average, 41 percent of the carbonaceous particles are less than 44 μm, whereas 83 percent, on average, of the mineral matter particles are less than 44 μm.

2. A considerable similarity in particle size distribution was found among the eleven Eastern samples. The two Western samples, however, were found to have quite different size distributions, probably due to differences in the mineralogy and in the sampling procedures.

3. Typically, the size distributions for the mineral matter tend to be bimodel, probably due to the presence of mixtures of "coarse" minerals (quartz, calcite, pyrite, etc.) and "fine" minerals (clays).

4. The size distributions of the mineral matter in the Eastern samples were found to be remarkably similar presumably

because of the similarity in their mineral content. The particle size distributions of the mineral matter from all eleven of these Eastern samples could be plotted as a narrow band with a standard deviation ranging from ±2.2 to ±9.7 percent depending on size. A composite size distribution shows that, on the average, 70, ±9.7 percent of the mineral matter is finer than 10 microns. The fineness of these materials is no doubt due to the presence of large amounts of clay minerals.

5. Similar composite size distributions for the carbonaceous fractions produced a standard deviation ranging from ±0.8 to ±15.9 percent. The average size distribution of the carbonaceous fraction indicates this material to be much coarser than is the mineral matter fraction. By comparison with the mineral matter fraction, the carbonaceous material averages only 21.2, ±7.3 percent finer than 10 microns.

6. For most of the samples, the high clay content completely dominated the size characteristics of the mineral matter fraction and strongly influenced the overall size characteristics of the blackwater solids.

C. Surface Properties

The third area of investigation was a study of the surface properties of the principal mineral and carbonaceous constituents.

A Zeta Meter was used to determine the electrophoretic mobility of these constituents as a function of pH.

1. Hydronium and hydroxyl ions are potential determining ions for coal and the silicate mineral constituents in blackwater. These two mineral categories (coal and silicates) typically account for about 90% of the particulate matter found in blackwater.

2. Pyrite and the carbonate minerals, mostly calcite, are the only important constituents found in blackwater for which these ions are not directly the potential determining ions. These minerals are indirectly affected by the concentration of H^+ and OH^- ions, however, because of the effect of pH on their potential determining ions through the $CO_2\text{-}HCO_3^-, CO_3^=$ and $H_2S\text{-}SH^-\text{-}S^=$ equilibria and through precipitation of metal ions by hydroxyl ions.

3. The point of zero charge, PZC, for the silicate minerals is usually below a pH of 4.

4. The surface properties of the illitic group of clay minerals was highly variable reflecting the high degree of structural and compositional variation in this class of clay minerals. For some illites the PZC occurred at pH 2-3 while for others no PZC was found and the particles maintained a negative potential over the entire range studied, pH 2-10.

5. Manipulation of the pH of blackwater suspensions will have a strong influence on the zeta potential of the contained mineral matter, and offers a means of controlling the agglomeration of this mineral matter. The agglomeration of most of the mineral matter in blackwater, the silicates, should be favored as the pH of the suspension is lowered.

It is not to be inferred that pH control would be the only means, or even the preferred means, of achieving flocculation of the particulate matter in blackwater. In practice, the use of inorganic and organic flocculating agents such as lime, alum, starch, and polyacrylamides would usually be the preferred method of flocculation.

6. Since most of the mineral matter in blackwater is clays, the surface properties of these clay minerals will exert a major influence on the surface properties of the suspension as a whole. This effect is further magnified because of the small particle size and high surface area of the clays.

7. The large carbonaceous (coal) content in most of the blackwater samples suggests that the surface properties of this coal will also be an important factor in determining the bulk properties of the suspension and the blackwater treatment process.

8. The fresh coal samples tested have a PZC between pH 3 and 7, with the PZC decreasing to pH 2 or below as the surface of the

coal becomes oxidized. The zeta potential of most coals is negative for alkaline solutions and decreases in magnitude as the pH is lowered.

The surface properties of the carbonaceous constituents of blackwater will depend on a number of factors such as rank, lithotype, degree of oxidation, and the chemistry of the blackwater solution.

9. In actual practice one would expect the carbonaceous particles contained in blackwater to have surface properties much closer to those of oxidized coal than to the fresh coal.

D. Characterization of a Typical Eastern Blackwater Sample

The characteristics of an average Eastern blackwater sample are shown in Table 17.

Table 17. Characteristics of a typical eastern blackwater sample.

Solid Material

	Mineral	Carbonaceous	Total
Weight, Percent	40.6	59.4	100.0
Ash, Percent	84.3	10.9	41.0
Sulfur, Percent	1.97	1.51	1.68

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
55	11	15	12	4	4

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	86	44	59
1	22	3	11

Surface Properties of the Principal Constituents (coal and silicates)

Potential Determining Ions	H^+ OH^-
Point of Zero Charge	Less than pH 5

VI. RECOMMENDATIONS FOR FUTURE STUDY

This work, while accomplishing much in the area of characterizing blackwater, opened up several new areas worthy of future study. The following suggestions are given for the extension of this research:

1. Characterization of effluent from different unit operations, especially jigs, heavy media vessels, cyclones, tables, and froth flotation.

2. An analysis of the fine particulate material that tends to remain suspended in the thickener overflow at different coal preparation plants.

3. Comparison of the surface properties of solid material in the primary effluent from plants having froth flotation with that of plants not having flotation.

4. Analyses of the particle size of thickener underflow from preparation plants using similar treatment methods but treating coal from different seams.

5. Determination of the mineral composition of the strata bordering different coal seams for purposes of making a direct

comparison with the mineral composition of their respective blackwaters.

6. Investigate how the information obtained in this study relates to obtaining a more efficient method of treating blackwater, especially in the areas of flocculation and filtration.

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APPENDIX A

STANDARD X-RAY DIFFRACTION GRAPHS FOR QUANTIFICATION OF THE MINERAL MATTER FRACTION FOUND IN BLACKWATER

Several of the important minerals were quantified using peak height of a characteristic x-ray diffraction peak of that particular mineral. A set of graphs (Figures A.1-A.6) relating peak height to the mineral content was used for this quantification. The mineral content was varied by adding known amounts of powdered glass, an amorphous substance which serves as a diluent. The mixtures were mounted and x-rayed using the procedure outlined in Section III.B.3. The characteristic peak, source, and impurities of each standard are listed in Table A.1.

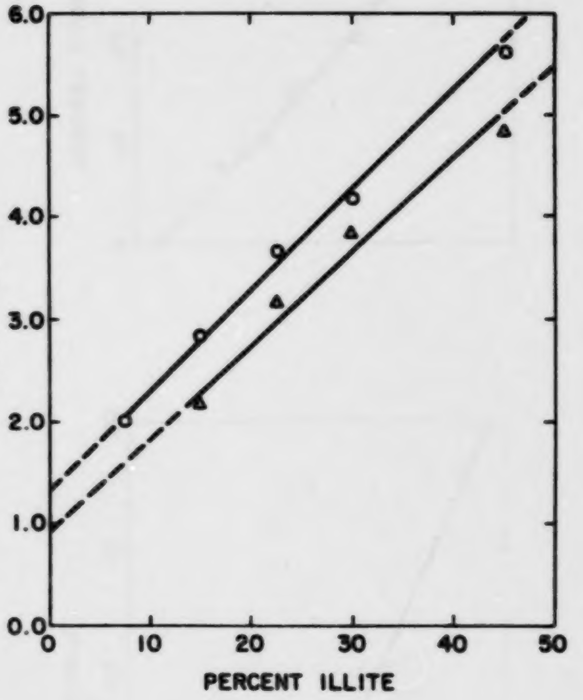

Figure A.1. Standard x-ray diffraction pattern for illite.

2.57 Å Peak
4.48 Å Peak

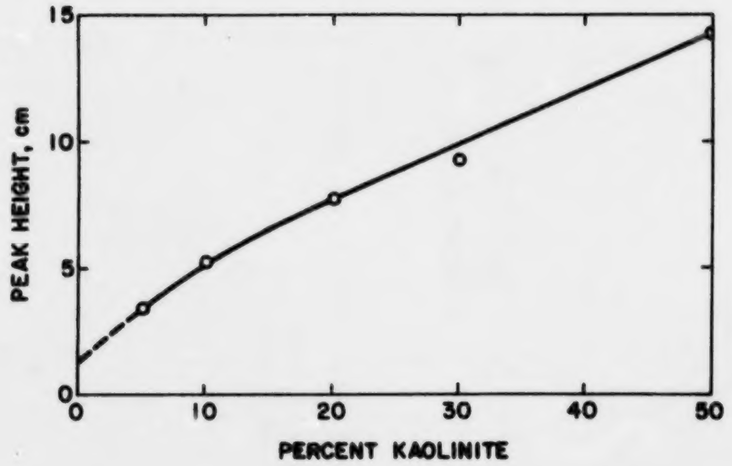

Figure A.2. Standard x-ray diffraction pattern for kaolinite.
3.57 Å Peak

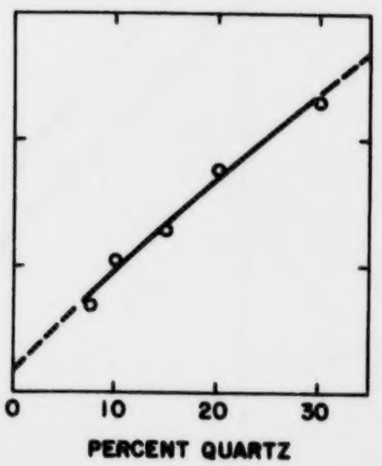

Figure A.3. Standard x-ray diffraction pattern for quartz.
1.82 Å Peak

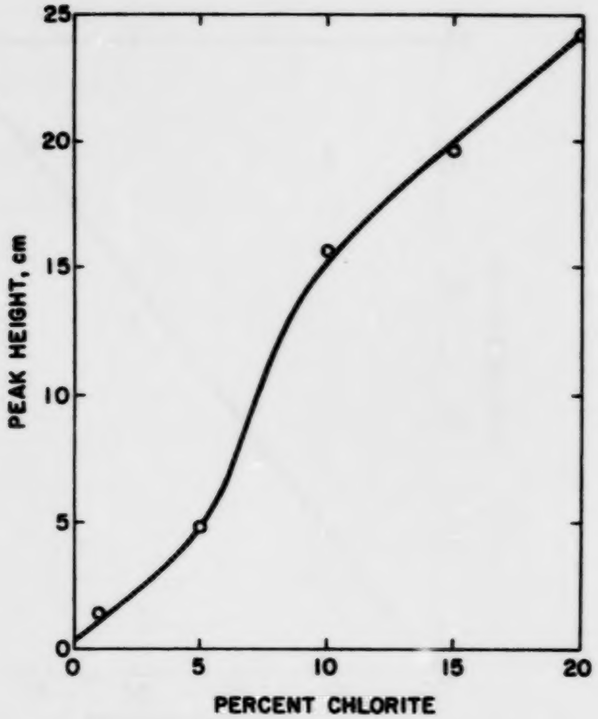

Figure A.4. Standard x-ray diffraction pattern for chlorite.
3.55 Å Peak

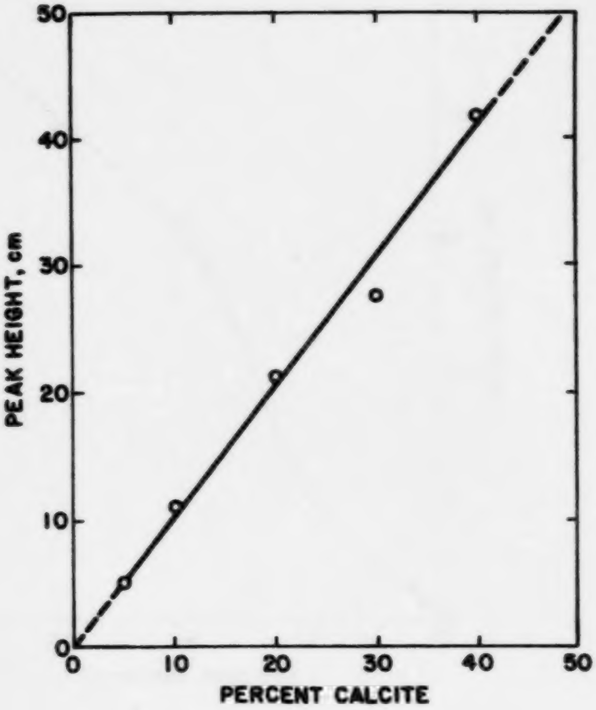

Figure A.5. Standard x-ray diffraction pattern for calcite.
3.04 Å Peak

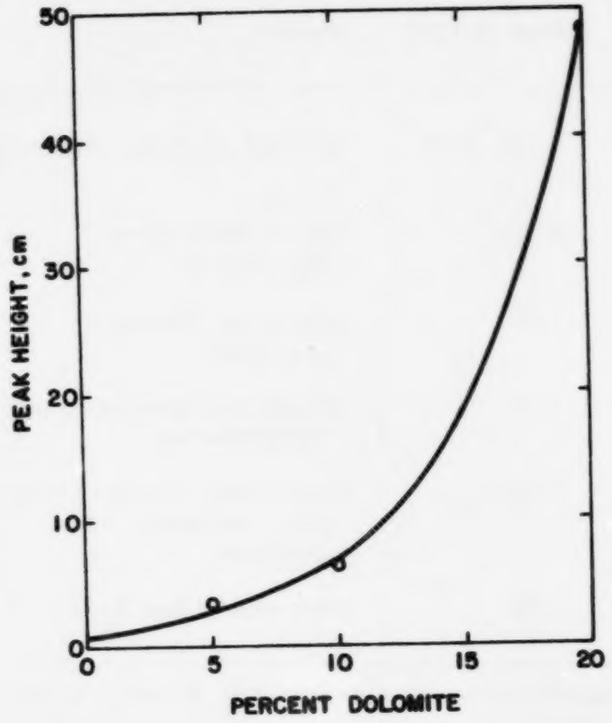

Figure A.6. Standard x-ray diffraction pattern for dolomite.
2.88 Å Peak

Table A.1. Characteristic peaks, source, and impurities found in the blackwater samples.

Mineral	Peak A (19)	Source	Impurities
Illite	4.48, 2.57	API[a]#35 Fithian, Illinois	17% quartz 8% calcite
Kaolinite	3.57	API #9 Mesa Alta, New Mexico	---
Chlorite	3.55	Calaveras County, California	---
Calcite	3.04	Valentine, Centre County Pennsylvania	---
Quartz	1.82	Castastone Products Company, Inc., Raleigh, North Carolina	---
Dolomite	2.88	Thornwood, New York	---

[a] API, American Petroleum Institute Clay Mineral Standards, Project No. 49.

APPENDIX B

X-RAY DIFFRACTION ANALYSIS OF THE MINERAL MATTER FRACTION FOUND IN BLACKWATER

Following separation of the solids found in blackwater into a carbonaceous and a mineral matter fraction, the mineral composition of this latter fraction was determined for each sample by x-ray diffraction using two different techniques.

In the first method the mineral composition of each blackwater sample was determined by performing x-ray diffraction analysis on a representative sample of the mineral matter from each sample. This sample is called the composite sample.

In the second method the mineral matter was separated into layers by centrifuging and each layer was weighed and analyzed by the x-ray method. From these data the total mineral composition could be calculated. Specific details of the procedure are given in Section III.B.3.

The following tables give the primary mineralogical analysis of each layer, as determined by x-ray techniques, used to calculate the mineral content of each sample shown in Tables 9-11.

Table B.1. Sample, Pi. W Pa 1.

Layers	Top	2nd	3rd	4th	Total	Composite
Weight %	6	17	33	44	100	---
Illitic[a] 4.48 Å	65	82	66	40	57	45
2.57 Å	63	63	58	33	48	43
Kaolinite	24	18	15	11	14	11
Chlorite	5	4	3	4	4	3
Calcite	3	4	10	14	10	18
Quartz	1	5	17	30	20	14
Pyrite	---	---	---	---	3	2

[a] Identification:
Dominate: Slightly interstratified illite-montmorillonite.
Significant: Illite

Table B.2. Sample, L.K. C Pa 2.

Layers	Top	Bottom	Total	Composite
Weight %	32	68	100	---
Illitic[a] 4.48 Å	56	44	48	41
2.57 Å	61	33	42	39
Kaolinite	30	14	19	15
Chlorite	4	4	4	3
Calcite	11	14	13	11
Quartz	15	16	16	11
Pyrite	---	---	4	4

[a] Identification:
Dominate: Illite, moderately interstratified illite-montmorillonite.
Significant: Montmorillonite.
Carbonaceous: ∿3%.
Other Minerals: Rutile ∿1%.

Table B.3. Sample, L.K. C Pa 3.

Layers	Top	Bottom	Total	Composite
Weight %	69	31	100	---
Illitic[a] 4.48 Å	54	49	52	44
2.57 Å	57	27	48	47
Kaolinite	20	19	20	20
Chlorite	2	4	3	4
Calcite	5	8	6	12
Quartz	12	15	13	10
Pyrite	---	---	3	3

[a] Identification:
Dominate: Illite.
Significant: Slightly interstratified illite-montmorillonite.
Carbonaceous: ∿5%.

Table B.4. Sample, L.F. C Pa 4.

Layers	Top	2nd	3rd	4th	Total	Composite
Weight %	15	20	36	29	100	---
Illitic[a] 4.48 Å	66	40	25	25	34	28
2.57 Å	39	34	2	12	18	23
Kaolinite	10	11	1	5	6	8
Chlorite	4	3	3	2	3	2
Calcite	5	10	28	22	19	23
Quartz	0	11	10	5	7	9
Pyrite	---	---	---	---	3	3

[a] Identification:
Dominate: Highly interstratified illite-montmorillonite.
Significant: Illite, montmorillonite.

Table B.5. Sample, Po. M WVa 5.

Layers	Top	2nd	3rd	4th	Total	Composite
Weight %	23	29	30	18	100	---
Illitic[a] 4.48 Å	50	42	53	75	53	46
2.57 Å	48	42	64	75	56	55
Kaolinite	8	5	11	11	9	13
Chlorite	5	5	6	6	6	6
Calcite	3	5	11	9	7	5
Quartz	5	11	26	20	16	18
Pyrite	---	---	---	---	1	1

[a] Identification:
Dominate: Illite.
Other Minerals: Dolomite, rutile, siderite, all ∿1%.

Table B.6. Sample, Po. W WVa 6.

Layers	Top	Bottom	Total	Composite
Weight %	27	73	100	---
Illitic[a] 4.48 Å	60	38	44	46
2.57 Å	58	42	46	49
Kaolinite	15	18	17	13
Chlorite	6	6	6	4
Calcite	8	17	15	16
Quartz	6	20	16	11
Pyrite	---	---	1	1

[a] Identification:
Dominate: Illite.
Significant: Slightly interstratified illite-montmorillonite, montmorillonite.
Other Minerals: Rutile, siderite, all ∿1%.

Table B.7. Sample, Pi./L.F. H Oh 7.

Layers	Top	Bottom	Total	Composite
Weight %	26	74	100	---
Illitic[a] 4.48 Å	57	29	36	49
2.57 Å	51	32	37	34
Kaolinite	12	5	7	6
Chlorite	3	2	2	3
Calcite	8	15	13	11
Quartz	18	16	17	12
Pyrite	---	---	10	10

[a] Identification:
Dominate: Moderately interstratified illite-montmorillonite.
Significant: Illite, montmorillonite.
Carbonaceous: ∿10%.
Other Minerals: Rutile.

Table B.8. Sample, E L Ky 8.

Layers	Top	Bottom	Total	Composite
Weight %	9	91	100	---
Illitic[a] 4.48 Å	58	51	52	48
2.57 Å	65	58	59	62
Kaolinite	9	9	9	6
Chlorite	6	7	7	6
Calcite	2	0	0	0
Quartz	2	15	14	12
Pyrite	---	---	1	1

[a] Identification:
Dominate: Illite.
Significant: Interstratified illite-montmorillonite, montmorillonite.
Other Minerals: Feldspar, rutile, siderite, all ∿1%.

Table B.9. Sample, Pr. J Ala 9.

Layers	Top	Bottom	Total	Composite
Weight %	62	38	100	---
Illitic[a] 4.48 Å	66	50	60	59
2.57 Å	62	56	60	61
Kaolinite	7	6	7	6
Chlorite	5	4	5	3
Calcite	0	0	0	0
Quartz	9	20	13	14
Pyrite	---	---	1	1

[a] Identification:
Dominate: Illite.
Significant: Slightly interstratified illite-montmorillonite, montmorillonite.
Other Minerals: Dolomite, ~5%.

Table B.10. Sample, I6/5 J Ill 10.

Layers	Top	2nd	3rd	4th	Total	Composite
Weight %	7	17	33	43	100	---
Illitic[a] 4.48 Å	75	72	56	23	46	60
2.57 Å	69	66	56	23	44	42
Kaolinite	5	6	6	10	8	3
Chlorite	0	0	0	0	0	0
Calcite	2	2	10	31	17	26
Quartz	0	1	26	24	19	22
Pyrite	---	---	---	---	4	9

[a] Identification:
Dominate: Highly interstratified illite-montmorillonite.
Significant: Illite.

Table B.11. Sample, I6 W Ind 11.

Layers	Top	2nd	3rd	4th	Total	Composite
Weight %	3	12	44	40	100	---
Illitic[a] 4.48 Å	57	62	60	57	58	65
2.57 Å	62	48	78	60	66	52
Kaolinite	17	11	19	19	17	10
Chlorite	4	3	5	5	5	3
Calcite	3	2	8	9	7	7
Quartz	9	0	20	30	21	22
Pyrite	---	---	---	---	6	6

Table B.12. Sample, B.D. L Wa 12.

Layers	Top	2nd	3rd	4th	Total
Weight %	7	20	31	42	100
Montmorillonite	100	90	80	50	70
Feldspar	0	10	20	50	30

Carbonaceous: ~5%.

Table B.13. Sample, S/L.S. Ut 13.

Layers	-400 Mesh	+400 Mesh	Total
Weight %	50	50	100
Montmorillonite	48	15	31
Kaolinite	16	32	24
Quartz	9	15	12
Calcite	15	19	17
Dolomite	12	17	14
Pyrite	---	---	2

Carbonaceous: ∿10 %.
Other Minerals: Feldspar ∿1%.

APPENDIX C

POTASSIUM ANALYSIS OF THE MINERAL MATTER FRACTION FOUND IN BLACKWATER FIRST ELEVEN SAMPLES

The potassium content of the mineral matter fraction from the Eastern blackwater samples was used as one method of quantifying the illite content. The potassium content of the samples was determined using atomic absorption (22). The average K_2O content of the two Fithian, Illinois samples was used as a standard value to estimate the illite content in the mineral matter fraction of the various blackwater samples. These standard illite samples were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York, at different times, and they are listed as the API #35 sample and the 25 pound sample. The purity of the two samples was determined using the x-ray diffraction procedure outlined in Section III.B.3 and the "difference" method. The mineral composition of the two illite standards was as follows: API #35-75% illite, 17% quartz, and 8% calcite; 25 lb material-80% illite, and 20% quartz. From this average K_2O content of standard illite, 5.12%, the illite content of the mineral matter fraction from each of the blackwater samples was calculated. The K_2O analytical data and the calculated percentage of illite in each sample is shown in Table C.1.

The K_2O content of the two standards was corrected for contamination by other minerals using the following procedure:

API #35 contained 75% illite and 3.95% K_2O

$$100\% \text{ illite} = \frac{3.95\% \text{ } K_2O}{0.75} = 5.26\% \text{ } K_2O$$

25 lb sample contained 80% illite and 3.98% K_2O

$$100\% \text{ illite} = \frac{3.98\% \text{ } K_2O}{0.80} = 4.98\% \text{ } K_2O$$

The average K_2O content of the illite clay in these two standard samples is 5.12% which was used to determine the illite content in the mineral matter fraction from the blackwater samples.

$$\text{Percent illite in mineral matter} =$$

$$\text{Percent } K_2O \text{ in sample} \div (5.12) \times 100$$

These samples had been collected in the field by Ward's from the same location but the two samples were taken several years apart. Thus, some sample variability is to be expected.

Table C.1. Quantitative atomic absorption determination of K_2O.

Sample	% K_2O	% Illite[a]
Pi. W Pa 1	1.90	37
L.K. C Pa 2	1.70	34
L.K. C Pa 3	1.75	34
L.F. C Pa 4	2.02	39
Po. M. WVa 5	3.62	71
Po. W. WVa 6	3.45	68
Pi./L.F. H Oh 7	1.75	37
E L Ky 8	4.12	80
Pr. J Ala 9	3.44	67
I6/5 J Ill 10	2.44	47
I6 W Ind 11	3.05	60
API #35 Illite	3.95	Standard
25 lb Sample Illite	3.98	Standard

[a] Based on 100% illite = 5.12% K_2O.

APPENDIX D

PARTICLE SIZE ANALYSES

The size analysis of the blackwater samples was determined using the procedure outlined in Section III.C. The separate analyses of each minus 400 material using the MSA-Whitby device were used to determine the size distribution of that material. The values from these two tests were then plotted on Rosin-Rammler paper and a smooth curve was drawn through the points. This size distribution was then adjusted from a base of 100 percent to a percentage that equaled the minus 400 mesh material contained in the sample. These values and the sieve values were then used to produce the combined size distribution of that material shown in Figures 5-15. Two samples were also analyzed using the Micromeritics Sedigraph (Figures D.1 and D.2) in which only the mineral matter portion was examined. Tables D.1 to D.6 give particle size data for both mineral matter and carbonaceous material for all the blackwater samples examined while Table D.7 gives mean particle size data of eleven eastern blackwater samples.

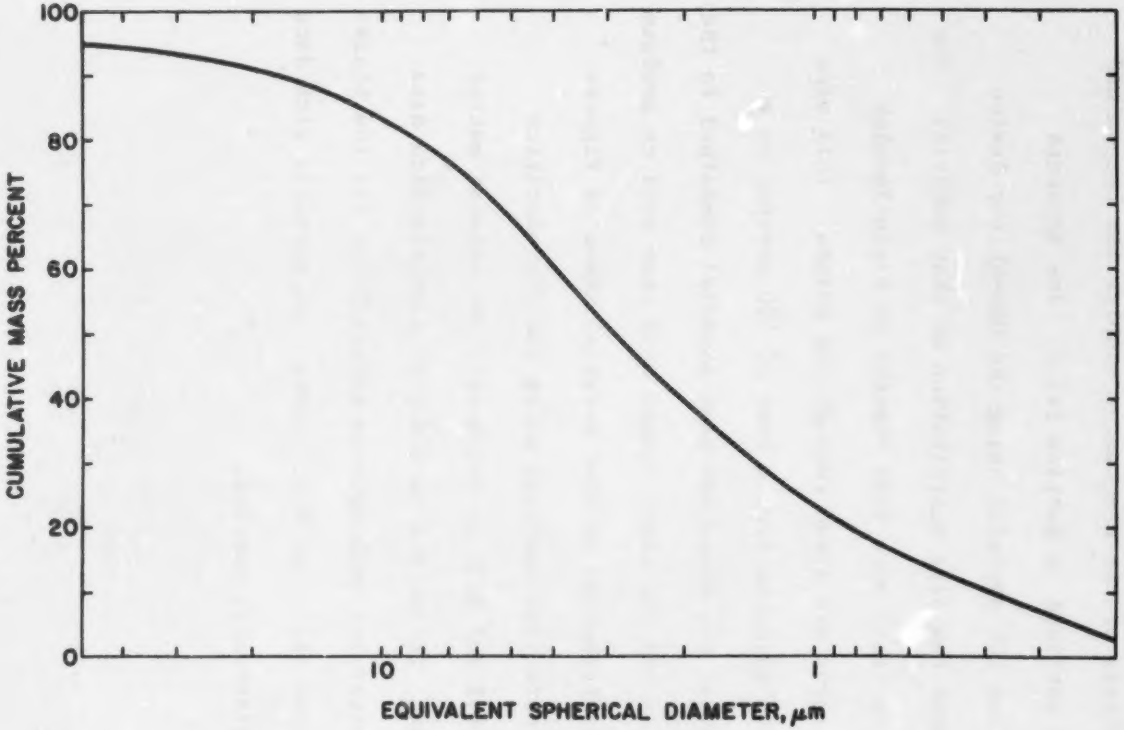

Figure D.1. Sedigraph particle size distribution, sample no. E L Ky 8.

Sample Identification: Mineral matter (-400 mesh)
Density: 2.7 g/cc
Liquid: Water
Temperature: 33°C
Rate: 465
Start Diameter: 50 μm

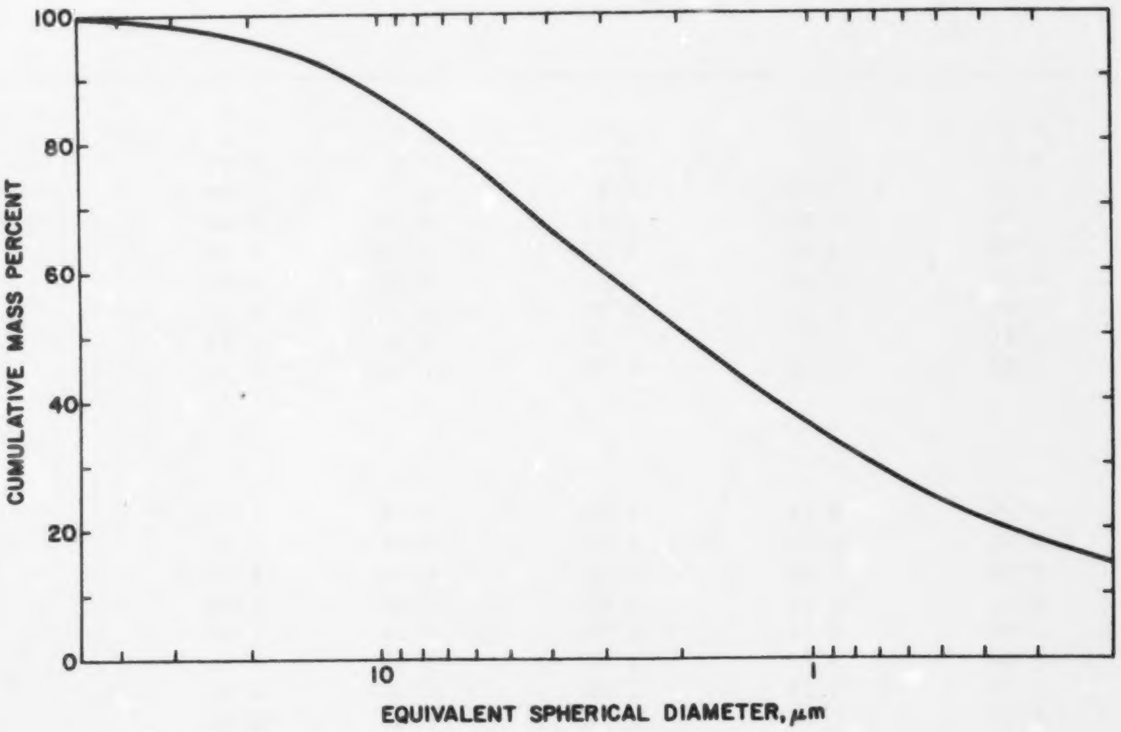

Figure D.2. Sedigraph particle size distribution, sample no. S/L./S. Ut 13.

Sample Identification: Mineral matter (-400 mesh)
Density: 2.7 g/cc
Liquid: Water
Temperature: 33°C
Rate: 465
Start Diameter: 50 μm

Table D. 1. Particle analysis of mineral matter fraction cumulative percent finer.

Size, Sieve	Pi WPa 1	L.K.C. Pa 2	L.K.C. Pa 3	L.F.C. Pa 4	Po MWVa 5	Po WWVa 6
14	100.0	100.0	100.0	100.0	100.0	100.0
14 x 20	100.0	99.9	99.2	99.9	100.0	99.8
20 x 28	100.0	99.7	97.4	99.6	99.8	99.7
28 x 35	99.9	99.5	93.5	99.1	99.6	99.3
35 x 48	99.9	99.2	88.5	97.5	99.2	98.3
48 x 65	99.7	98.6	85.2	94.8	98.4	96.3
65 x 100	99.1	97.1	82.3	90.6	96.5	93.4
100 x 150	98.1	95.3	80.2	87.2	94.5	91.4
150 x 200	95.8	90.0	75.9	80.9	90.8	87.6
200 x 270	94.4	86.6	73.5	77.9	89.1	85.4
270 x 400	92.6	81.7	69.9	73.8	87.1	82.2
Subsieve (μm)						
20	91.3	80.6	64.7	65.6	83.0	78.2
10	82.5	74.0	55.7	50.9	69.9	69.9
5	68.9	61.9	40.5	45.2	52.7	51.8
3	55.6	50.1	32.0	34.8	41.3	36.9
2	47.8	44.7	27.4	29.4	31.7	28.2
1	29.1	27.4	15.7	18.5	18.3	16.2
0.5	18.6	17.5	8.7	11.7	10.3	8.3
0.3	12.2	9.8	4.6	7.3	5.4	6.9
0.2	7.6	4.0	1.7	3.0	3.4	3.8

Table D.1. Continued.

Size, Sieve	Pi/LFHOh 7	ELKy 8	PrJala 9	I6/5JI11 10[a]	I6WInd 11[a]
14	100.0	100.0	100.0	---	---
14 x 20	99.4	90.7	99.9	---	---
20 x 28	99.0	99.4	99.8	---	---
28 x 35	98.6	99.3	99.7	99.5	---
35 x 48	98.1	99.1	99.5	98.2	99.4
48 x 65	97.4	98.8	99.2	96.1	97.9
65 x 100	96.7	98.3	98.4	93.1	95.8
100 x 150	96.2	97.8	97.5	88.9	94.2
150 x 200	94.5	96.1	95.1	84.6	93.1
200 x 270	92.7	94.9	94.1	82.2	92.6
270 x 400	88.3	92.8	92.0	78.2	90.8
Subsieve (μm)					
20	80.2	91.5	83.0	76.1	86.9
10	69.5	83.6	69.9	69.2	75.4
5	50.7	68.5	52.7	60.1	56.0
3	38.8	51.1	41.3	50.9	40.0
2	30.1	40.8	31.7	41.7	34.2
1	19.2	25.0	18.3	28.0	22.6
0.5	11.5	12.2	10.3	17.5	3.9
0.3	6.6	7.9	5.4	0.5	---
0.2	3.1	5.3	3.4	---	---

[a] Size analysis by Michael F. Placha (30).

T.ble D.1. Continued.

Size, Sieve	B.D.L.Wa 12[a]	S/LS Ut 13
14	---	---
14 x 20	---	---
20 x 28	---	99.6
28 x 35	---	83.9
35 x 48	99.4	67.8
48 x 65	98.7	60.1
65 x 100	97.7	55.9
100 x 150	96.2	53.7
150 x 200	93.7	51.6
200 x 270	92.3	50.8
270 x 400	90.5	50.0
Subsieve (μm)		
20	89.7	47.9
10	82.5	41.8
5	65.1	33.0
3	57.4	26.2
2	51.9	22.5
1	31.4	14.3
0.5	20.5	9.9
0.3	12.9	6.9
0.2	6.6	4.7

---

[a] Size analysis by Michael F. Placha (30).

Table D.2. Particle analysis of carbonaceous fraction cumulative percent finer.

Size, Sieve	Pi WPa 1	L.K.C. Pa 2	L.K.C. Pa 3	L.F.C. Pa 4	Po MWVa 5
+ 14	---	---	---	---	---
14 x 20	---	99.8	99.3	99.8	---
20 x 28	98.4	98.3	93.9	99.2	99.1
28 x 35	97.5	94.5	83.3	96.1	96.7
35 x 48	93.5	88.6	72.7	88.7	92.8
48 x 65	89.5	81.3	96.3	81.4	89.2
65 x 100	85.8	72.3	57.6	74.3	84.6
100 x 150	82.4	62.8	49.0	67.1	79.8
150 x 200	75.9	53.8	42.7	59.3	71.9
200 x 270	70.7	48.3	37.7	47.9	61.5
270 x 400	64.6	40.3	32.9	43.3	56.1
Subsieve (μm)					
20	50.8	32.5	27.0	37.8	46.1
10	33.7	19.6	16.7	24.8	29.1
5	22.4	12.8	11.0	15.8	19.6
3	17.1	8.4	7.1	12.7	13.3
2	13.3	5.6	5.3	9.7	10.1
1	6.4	2.6	2.5	4.9	5.0
0.5	2.4	0.3	0.6	2.4	1.4

Table D.2. Continued.

Size, Sieve	Po WWVa 6	Pi/LFHOh 7	ELKy 8	PrJAla 9	I6/5JI11 10[a]
+ 14	99.8	99.9	99.8	99.8	---
14 x 20	99.5	99.7	99.2	99.7	99.9
20 x 28	98.1	98.9	97.7	99.4	99.8
28 x 35	94.6	96.6	95.9	98.3	99.6
35 x 48	88.7	86.6	91.8	95.3	96.3
48 x 65	82.6	66.8	84.1	91.1	84.9
65 x 100	75.6	44.6	73.6	85.5	67.8
100 x 150	68.3	29.8	64.0	77.8	54.2
150 x 200	61.2	21.8	56.0	68.0	48.6
200 x 270	56.6	18.7	51.4	60.0	38.1
270 x 400	49.2	15.4	44.5	49.9	26.2
Subsieve (μm)					
20	38.9	12.9	36.9	35.3	20.6
10	24.2	8.4	22.9	22.9	11.1
5	14.2	5.1	13.6	13.5	6.8
3	8.5	3.6	10.0	9.4	6.0
2	5.3	2.4	7.2	6.7	5.7
1	2.3	1.1	2.9	2.6	0.7
0.5	0.0	0.4	1.1	1.2	0.1

---

[a] Size analysis by Michael F. Placha (30).

Table D.2. Continued.

Size, Sieve	I6WInd 11[a]	B.D.L.Wa 12[a]	S/LS Ut 13
+ 14	---	---	---
14 x 20	99.5	---	---
20 x 28	96.4	---	99.9
28 x 35	87.5	90.0	98.4
35 x 48	74.2	71.0	92.9
48 x 65	63.7	64.0	84.4
65 x 100	54.6	56.0	49.5
100 x 150	46.8	44.0	48.3
150 x 200	39.7	31.0	44.4
200 x 270	35.6	24.0	42.0
270 x 400	30.3	11.0	40.1
Subsieve (μm)			
20	25.1	---	27.0
10	19.6	---	16.0
5	10.7	---	9.7
3	7.2	---	6.5
2	5.3	---	4.7
1	2.7	---	2.3
0.5	0.9	---	1.5

---

[a] Size analysis by Michael F. Placha (30).

Table D.3. MSA sedimentation particle size analysis procedure for mineral matter.

Sample Material--mineral
Sample Density--2.7 (tails)
Feeding Liquid--distilled water
Dispersing Agent--0.15 calgon, 50 ppm bleach
Room Temperature--23°C
Tube Size--0.75 mm
Sedimentation Liquid--distilled water
Wetting Agent--Aerosol OT

$R_o = 3.3$ cm

$R_2 = 13.3$ cm

$K_g = 9.31 \times 10^4$

d	RPM	Time (sec)	Corr. Time (sec)
40	Gravity	58	58
20	Gravity	233	233
10	Gravity	931	931
5	600	77	86
3	1200	55	65
2	1200	111	121
1	3600	67	106
0.5	3600	267	306
0.3	3600	637	676
0.2	3600	1235	1274

Note:
After the 0.2 μm value was determined, the sample was repeatedly centrifuged at 3600 RPM for 20 minutes until a final height was obtained.

Table D.4. MSA sedimentation particle size analysis of mineral matter fraction cumulative weight percent finer.

Sample Size (µm)	PiWPa 1		L.K.C.Pa 2		L.K.C.Pa 3		L.K.C.Pa 4		PoMWVA 5		PoWWVa 6		Pi/LFHOh 7	
	Test		Test		Test		Test		Test		Test		Test	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
40	---	---	---	---	---	---	99.6	---	---	---	---	---	---	---
20	98.9	98.6	97.2	98.7	92.5	93.3	88.9	90.9	95.3	96.4	95.2	97.1	90.9	95.4
10	90.7	89.0	90.6	90.6	71.7	79.6	69.0	77.2	80.2	81.0	85.0	88.8	72.6	78.7
5	73.4	74.4	73.6	75.8	57.9	61.3	61.3	64.6	60.5	60.5	63.1	66.3	57.5	59.2
3	59.4	60.0	64.2	61.4	45.8	48.4	47.2	52.8	47.4	47.0	44.9	52.2	44.0	46.5
2	51.5	51.6	52.4	54.7	39.2	40.0	39.9	42.9	36.4	36.4	36.9	44.3	34.1	35.5
1	35.9	31.5	35.8	33.6	22.5	23.1	25.1	26.0	21.0	20.6	18.2	23.1	21.8	22.0
0.5	20.3	20.1	24.0	21.5	12.5	12.0	15.9	16.5	11.9	10.3	10.2	14.3	13.1	12.1
0.3	11.7	13.2	15.7	12.1	6.7	5.3	10.0	9.4	6.3	7.1	4.8	8.4	7.5	6.7
0.2	6.8	8.2	5.9	5.0	2.5	0.4	4.1	5.1	4.0	3.6	1.0	4.7	3.6	2.8

Table D.4. Continued.

Sample Size (μm)	ELKy 8		PrJAla 9		I6/5JIl1 10[a]		16WInd 11[a]		BDLWa 12[a]		S/LS Ut 13	
	Test		Test		Test		Test		Test		Test	
	1	2	1	2	1	2	1	2	1	2	1	2
40	---	---	---	---	---	---	---	---	---	---	---	---
20	98.6	99.0	93.4	88.9	97.1	---	95.7	---	99.2	99.0	95.9	96.4
10	90.1	95.3	87.5	81.8	88.3	---	83.0	---	92.9	89.4	83.7	84.9
5	73.8	79.1	72.0	68.5	76.3	---	61.7	---	73.3	70.4	66.0	64.1
3	55.1	66.3	60.7	56.5	64.9	---	44.7	---	60.8	65.9	52.5	51.0
2	46.3	57.3	50.7	48.5	53.2	---	37.7	---	54.4	60.3	45.0	39.5
1	23.4	29.4	37.4	32.5	35.7	---	24.9	---	33.3	36.0	28.6	22.4
0.5	13.2	18.0	23.8	20.9	22.3	---	4.3	---	22.3	22.8	19.8	13.5
0.3	6.3	10.4	12.5	12.9	0.6	---	0.0	---	14.2	14.2	13.8	7.6
0.2	2.2	5.8	6.6	7.1	0.0	---	0.0	---	7.3	---	9.4	3.3

[a] Size analysis by Michael F. Placha (30).

Table D.5. MSA sedimentation particle size analysis procedure for carbonaceous material.

Sample Material--carbonaceous
Sample Density--1.5
Feeding Liquid--distilled water
Dispersing Agent--100 ppm bleach
Room Temperature--23°C
Tube Size--0.75 mm
Sedimentation Liquid--distilled water
Wetting Agent--aerosol OT

$R_o = 3.3$ cm

$R_2 = 13.3$ cm

$K_g = 3.15 \times 10^5$

d	RPM	Time (sec)	Corr. Time (sec)
40	Gravity	197	197
30	Gravity	257	257
25	Gravity	504	504
20	Gravity	788	788
10	600	65	74
8	600	57	66
5	1200	65	75
3	1200	194	204
2	1200	377	387
1	3600	227	266
0.5	3600	908	947
0.3	3600	2160	2199

Note:
After the 0.3 μm value was determined, the sample was repeatedly centrifuged at 3600 RPM for 20 minutes until a final height was obtained.

Table D.6. MSA sedimentation particle size analysis of carbonaceous fraction cumulative weight percent finer.

Sample Size (μm)	PiWPa 1		L.K.C.Pa 2		L.K.C.Pa 3		L.F.C.Pa 4		PoMWVa 5		PoWWVa 6		Pi/LFHOh 7	
	Test		Test		Test		Test		Test		Test		Test	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
40	---	98.7	---	99.6	99.2	99.6	99.0	99.7	98.6	---	---	99.6	---	99.7
30	99.0	95.5	---	---	97.1	98.3	98.0	98.5	97.3	98.9	---	97.0	98.8	99.2
25	86.3	81.4	---	---	90.1	91.4	92.6	93.3	90.4	89.2	---	87.0	91.1	92.3
20	78.7	74.8	60.5	80.7	84.5	85.3	85.5	87.4	82.6	82.3	79.2	70.4	83.8	87.2
10	52.2	47.5	56.6	48.7	52.4	54.3	59.5	57.3	54.1	52.0	49.3	45.2	54.4	55.8
8	45.7	38.7	---	---	48.9	48.3	54.4	50.9	45.0	45.1	---	42.6	46.7	48.7
5	34.7	34.8	30.1	31.9	34.5	33.2	40.2	36.6	34.9	32.5	33.5	24.8	33.2	39.6
3	26.5	24.9	22.6	20.8	22.2	25.4	32.4	29.5	24.8	23.8	20.5	17.4	23.6	27.4
2	20.6	18.3	16.8	13.9	16.8	19.8	24.0	22.5	17.4	22.4	10.8	11.7	18.2	21.9
1	10.0	10.6	6.6	6.6	8.0	7.8	7.4	6.4	11.0	9.0	3.2	4.8	7.7	10.8
0.5	3.8	3.7	0.4	0.9	1.9	1.3	5.7	2.6	3.2	2.5	0.0	0.8	2.7	6.6
0.3	0.7	0.5	0.0	0.0	0.3	0.0	0.7	0.3	0.0	1.1	0.0	0.0	0.3	4.3

Table D.6. Continued.

Sample Size (μm)	ELKy 8		PrJAla 9		I6/5JI11 10[a]		15WInd 11[a]		S/LS Ut 13	
	Test		Test		Test		Test		Test	
	1	2	1	2	1	2	1	2	1	2
40	---	99.7	97.2	99.6	98.5	97.6	91.2	---	96.3	95.9
30	---	---	---	---	97.0	95.5	---	---	91.1	91.0
25	---	89.1	---	---	90.9	85.0	---	---	78.0	77.6
20	85.5	83.0	70.8	75.7	81.8	76.1	82.8	---	67.5	69.0
10	53.8	51.6	42.7	46.0	45.8	39.4	64.7	---	39.9	39.9
8	---	45.2	---	---	43.2	36.0	---	---	33.9	33.6
5	30.9	30.7	27.1	27.2	28.8	23.6	35.3	---	24.4	23.9
3	20.6	22.6	18.9	18.8	24.6	21.2	23.9	---	20.2	16.4
2	17.7	16.3	13.5	13.4	24.2	19.8	17.6	---	16.3	11.9
1	6.3	6.7	5.3	5.0	3.0	2.9	8.8	---	5.8	3.7
0.5	2.6	2.4	2.5	2.5	0.0	1.4	2.9	---	3.9	1.9
0.3	---	---	1.4	0.8	0.0	0.0	0.0	---	1.8	0.0

[a] Size analysis by Michael F. Placha (30).

Note:

Sample BDLW 12 carboniferous material was not analyzed due to the small percentage, <11%, that was present as minus 400 mesh material.

Table D.7. Mean particle analysis of thickener underflow or slurry and feed eastern samples (Nos. 1 to 11).

	Cumulative Weight % Finer			
	Mineral Material		Carboniferous Material	
Size, Sieve	Mean	Std.Dev.	Mean	Std.Dev.
14	---	---	---	---
14 x 20	---	---	---	---
20 x 28	---	---	---	---
28 x 35	---	---	94.6	4.8
35 x 48	97.9	3.2	88.1	7.8
48 x 65	96.6	4.0	80.1	9.9
65 x 100	94.7	4.8	70.6	13.4
100 x 150	92.8	5.5	62.0	15.9
150 x 200	89.5	6.6	54.4	15.7
200 x 270	87.6	7.2	47.9	14.6
270 x 400	84.5	7.9	41.1	14.1
Subsieve (μm)				
20	80.1	8.8	33.1	11.0
10	70.0	9.7	21.2	7.3
5	55.4	8.9	13.2	5.0
3	43.0	7.7	9.4	3.7
2	35.2	7.1	7.0	2.9
1	21.7	4.9	3.1	1.7
0.5	11.9	4.4	1.0	0.8
0.3	6.1	3.6	---	---
0.2	3.2	2.2	---	---

APPENDIX E

TABULATION OF THE MINERALOGICAL AND PARTICLE SIZE CHARACTERISTICS OF EACH OF THE THIRTEEN BLACKWATER SAMPLES

Sample No. Pi W Pa 1

Solid Material

	Mineral	Carbonaceous	Total
Wt %	44.5	55.5	100
Ash %	86.1	10.2	44.0
S %	1.11	1.14	1.13

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
51	12	18	19	3	2

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	93	66	77
1	33	6.1	17

Sample No. LK C Pa 2

Solid Material

	Mineral	Carbonaceous	Total
Wt %	35.8	64.2	100
Ash %	79.3	9.2	34.3
S %	2.36	1.75	1.97

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
46	17	14	12	4	4

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	84	43	58
1	27	2.5	11

Sample No. LK C Pa 3

Solid Material

	Mineral	Carbonaceous	Total
Wt %	34.0	66.0	100
Ash %	81.8	11.9	35.7
S %	1.46	1.06	1.20

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
48	22	9	14	4	3

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	70	35	40
1	15	2.5	4

Sample No. LF C Pa 4

Solid Material

	Mineral	Carbonaceous	Total
Wt %	19.6	80.4	100
Ash %	87.9	14.4	28.8
S %	1.40	1.30	1.32

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
65	7	8	21	3	3

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	76	44	50
1	18	4.2	7

Sample No. Po M W Va 5

Solid Material

	Mineral	Carbonaceous	Total
Wt %	29.1	70.9	100
Ash %	87.5	12.6	34.4
S %	0.70	0.94	0.87

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
57	11	17	6	6	1

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	89	62	70
1	18	5.0	9

Sample No. Po W WVa 6

Solid Material

	Mineral	Carbonaceous	Total
Wt %	36.1	63.9	100
Ash %	86.2	12.1	38.9
S %	0.56	0.76	0.69

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
47	15	15	17	5	1

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	84	52	64
1	17	2.3	8

Sample No. Pi/LF. H Oh 7

Solid Material

	Mineral	Carbonaceous	Total
Wt %	15.9	84.1	100
Ash %	70.5	10.9	20.4
S %	5.23	2.26	2.73

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
37	7	15	12	3	10

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	90	16	28
1	19	1.1	4

Sample No. E L Ky 8

Solid Material

	Mineral	Carbonaceous	Total
Wt %	52.1	47.9	100
Ash %	87.1	10.8	50.6
S %	0.56	0.71	0.63

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
62	8	13	0	7	1

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	93	47	69
1	25	3.0	14

Sample No. Pr J Ala 9

Solid Material

	Mineral	Carbonaceous	Total
Wt %	27.7	72.3	100
Ash %	88.0	9.2	31.0
S %	0.59	1.12	0.97

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
64	7	14	0	4	1

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	93	54	65
1	43	2.8	14

Sample No. I 6/5 J Ill 10

Solid Material

	Mineral	Carbonaceous	Total
Wt %	81.0	19.0	100
Ash %	84.3	10.7	70.3
S %	4.54	2.92	4.28

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
49	6	21	22	0	9

Particle Size Analysis (weight percent less than)

Size (µm)	Mineral	Carbonaceous	Total
44	80	30	64
1	28	0.8	19

Sample No. I6 W Ind 11

Solid Material

	Mineral	Carbonaceous	Total
Wt %	71.1	28.9	100
Ash %	88.2	8.4	62.7
S %	3.14	2.67	2.65

Mineral Composition (weight percent)

Illitic	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
61	14	22	4	4	6

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	91	32	66
1	12	5.2	9

Sample No. BD L Wa 12

Solid Material

	Mineral	Carbonaceous	Total
Wt %	72.8	27.2	100
Ash %	79.5	42.5	69.4
S %	0.42	1.30	0.66

Mineral Composition (weight percent)

Montmorillonite	Feldspar
70	30

Particle Size Analysis (weight percent less than)

Size (µm)	Mineral	Carbonaceous	Total
44	91	16	86
1	31	--	31

Sample No. S/LS UT 13

Solid Material

	Mineral	Carbonaceous	Total
Wt %	49.9	50.1	100
Ash %	71.2	21.8	46.5
S %	1.22	1.14	1.18

Mineral Composition (weight percent)

Montmorillonite	Kaolinite	Quartz	Calcite	Chlorite	Pyrite
31	24	12	17	14	2

Particle Size Analysis (weight percent less than)

Size (μm)	Mineral	Carbonaceous	Total
44	51	40	45
1	14	2.3	9